SMITH'S
INORGANIC CHEMISTRY

SECOND REVISED EDITION

BY

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ALEXANDER SMITH

1865-1922

Professor Alexander Smith, formerly head of the department of chemistry at Columbia University and in 1911 President of the American Chemical Society, died in his native city of Edinburgh, Scotland, on September 8, 1922, after a long illness, at the age of 57 years. He was the son of Alexander W. and Isabella (Carter) Smith, his father being a well-known musician. He married, in 1905, Sara Bowles of Memphis, Tennessee, and is survived by her and by two children.

Preëminent in his later years as a teacher and writer of general and inorganic chemistry, Alexander Smith commenced his career as an organic chemist. After graduating from Edinburgh University with the degree of Bachelor of Science in 1886, he worked under von Baeyer at Munich, obtaining his degree of Doctor of Philosophy in 1889. He returned to Edinburgh University for one year as assistant in chemistry, but in 1890 he came to this country as Professor of Chemistry and Mineralogy in Wabash College. His work there soon attracted attention, and in 1894 he was called to assist in the development of the newly-founded University of Chicago. There he served for 17 years, during the last 8 of which he acted as Director of the Laboratories of General and Physical Chemistry. The present high standing of the department of chemistry in the University of Chicago is undoubtedly due in large measure to the administrative genius of Alexander Smith. In 1911 he was appointed to succeed Professor Chandler as head of the department of chemistry at Columbia University, where he remained until serious illness necessitated his retirement.

Few men have rendered more significant service to American chemistry. As a teacher, Alexander Smith in his prime had no equal, and his guiding principles have fortunately been put in permanent form in his famous series of text-books. It is no exaggeration to state that the first issue of his "Inorganic Chemistry" in 1906 inaugurated a revolution in methods of instruction in America, comparable only with that effected in Germany by Ostwald's "Lehrbuch der allgemeinen Chemie." Instead of a hodge-podge of

isolated facts, the student found in these volumes a clear and logical presentation of the fundamental principles of the science. A proper appreciation of the physicochemical aspects of each topic under discussion constitutes, indeed, one of the main features of Alexander Smith's text-books, and indicates clearly the strong influence exerted by Ostwald and his school upon his work. The success of Alexander Smith's methods may be estimated by the number of his followers; practically every modern inorganic chemistry is based upon his foundations. Not only have his volumes enjoyed phenomenal popularity in this country and in Great Britain, but they have been translated into many foreign languages, including even Russian and Chinese.

Alexander Smith devoted much attention also to the manifold practical details connected with the teaching of chemistry, and a great number of his addresses deal with various aspects of this branch of his labors, ranging all the way from methods of laboratory instruction in high-school chemistry to the administrative problems of a large university department. It will suffice here to refer to two such lectures: "The Rehabilitation of the American College, and the Place of Chemistry in it," printed in *Science*, **30**, 457 (1909), and "The Training of Chemists," an address delivered in Urbana at the opening of the Chemical Laboratory of the University of Illinois, printed in *Science*, **43**, 619 (1916). His educational insight was rarely, if ever, at fault, and as an administrator he was untiring.

In the line of research, Alexander Smith's most outstanding publications dealt with amorphous sulphur and the exact measurement of vapor pressures. His valuable contributions in these two fields were recognized by the Royal Society of Edinburgh in 1912 by the award of the Keith Prize and Medal. The main results obtained in his work up to that date, as announced by Sir William Turner in making the presentation, are summarized below.

"The work on sulphur was published in seven papers. At the time these investigations were begun, the published observations upon the behavior of melted sulphur were full of apparent inconsistencies, and could not be formulated in harmony with physicochemical theory.

"The first step was to settle the disputed question as to the relations of amorphous and soluble sulphur in the melt. Measurements of freezing points and of the corresponding proportions of amorphous sulphur in the freezing liquid showed that Raoult's law

held rigorously. This established the existence of liquid amorphous sulphur dissolved, but distinct from the melted soluble sulphur.

"The fact that melted sulphur, when kept at a given temperature, gives, on chilling, very inconstant proportions of amorphous sulphur was next investigated. It was discovered that the introduction of sulphur dioxide and other foreign substances greatly influenced the proportions. These foreign bodies were proved to act catalytically, and retard or hasten the change from amorphous to soluble sulphur. The establishment of this conclusion at once afforded a basis for explaining a large proportion of the apparent inconsistencies in the older as well as the more recent observations. In connection with this work, the proportions of amorphous sulphur present in equilibrium at various temperatures were measured.

"In the fifth paper, studies of some other peculiarities in the behavior of melted sulphur were described, and all the results were shown to harmonize with a theory of the relation of the two liquid forms as dynamic isomers.

"Precipitated sulphur was the subject of the sixth paper, and it was shown that, when first liberated, the sulphur consists of droplets of liquid amorphous sulphur. In presence of weak acids, or in neutral or alkaline solutions, this changes wholly to crystalline, soluble sulphur. In presence of active acids, the amount of amorphous sulphur surviving in the final product is proportioned to the concentration of the acid.

"In the seventh paper, the generally accepted melting points (or freezing points) of the various forms of sulphur, determined before the complex nature of the problem which such measurements involved was in the least suspected, were subjected to revision, and the correct values, in harmony with the theory, were given.

"The work on Vapor Pressures (carried out in collaboration with Professor A. W. C. Menzies) is described in seven papers. The first two deal with a simple device, named the 'submerged bulblet,' by which boiling points and vapor pressures of liquids and of non-fusing solids may be determined with the use of only minute amounts of material.

"In the third and fifth papers, forms of apparatus for the exact study of vapor pressures, and named respectively the static and dynamic 'isoteniscope,' are described. To ascertain the possibilities of the methods, values for water, which agree with the best previous determination, were obtained by the static method, and values for benzene and for ammonium chloride by the dynamic method.

"The fourth paper describes a determination of the vapor pressures of mercury. These were made because exact values were required for the subject of the sixth paper, and the existing results (*e.g.*, those of Regnault, Ramsay and Young, and others) were highly inconsistent with one another, and the methods used were open to serious criticism.

"The sixth paper deals with the constitution of calomel vapor, a matter long but inconclusively discussed by chemists. By making measurements of the vapor pressures of mercury, of calomel, and of a mixture of the two, and applying the laws of chemical equilibrium to the resulting data, it was shown conclusively that the vapor is wholly composed of mercury and corrosive sublimate. The close quantitative correspondence showed that in these measurements the order of accuracy was much higher than in any previous measurements of vapor pressures at elevated temperatures.

"The seventh paper shows that, as the laws of chemical equilibrium applied to the result of the preceding paper predict, calomel, when dried in the most rigorous manner, exercises, even at high temperatures, no measurable pressure whatever. This is the only successful experimental confirmation of a familiar and important application of the theory."

The continuation of the work on vapor pressures, as carried on at Columbia after 1912, dealt chiefly with the dissociation equilibria of the ammonium halides. It had been shown by Baker that when great precautions are taken to exclude moisture the vapor of ammonium chloride consists entirely of undissociated molecules, the molecular weight corresponding to the formula, NH_4Cl. When, however, a trace of moisture is present, as in the "ordinary" methods of drying the substance, Baker found that at a temperature of 350° the degree of dissociation into NH_3 and HCl, as indicated by the Dumas bulb method, appeared to be almost complete. A similar result was obtained by other investigators employing the Victor Meyer method as well as that of Dumas. Smith, after first pointing out the extremely important fact that in all previous density determinations the *unsaturated* vapor only had been investigated, proceeded to establish, by very careful measurements, exact density values for the *saturated* vapor, and showed conclusively that the dissociation did not exceed 67% for ammonium chloride between 280° and 330°. The other ammonium halides were found to exhibit considerably less dissociation.

The unexpected fact that the vapor pressures of "dried" and

"undried" ammonium chloride at the same temperature are identical, in spite of the difference in character of the vapor in equilibrium with the solid phase, was also subjected to close examination. While no final explanation was reached, the results obtained were of service in disproving certain hypotheses which had been advanced by other investigators regarding this phenomenon.

In 1911 Alexander Smith was elected President of the American Chemical Society. His presidential address, delivered at Washington, dwelt upon the achievements and discoveries of Lomonossov, an early Russian physical chemist, whose remarkable work in the middle of the eighteenth century had been entirely forgotten until his fellow-countryman Menschutkin reprinted his memoirs in 1904. The historical side of chemistry always had a strong attraction for Alexander Smith, and his views upon the conflicting claims of the various "discoveries" of oxygen have been the center of considerable comment.

Other distinctions bestowed upon him were membership of the National Academy of Sciences and honorary membership of the Spanish Society of Physics and Chemistry.

In 1919 his *alma mater,* the University of Edinburgh, awarded him the degree of LL.D. He was introduced at the graduation ceremonies as follows: "A most distinguished graduate of our own University, Professor Smith has risen to the rank of a super-chemist in the United States, head of a department embracing many specialized professorships, and director of one of the most important laboratories in the new world. We congratulate Columbia University on the possession of a teacher and investigator of such rare ability, and we congratulate ourselves on the opportunity of laureating an alumnus whose success reflects no little luster on the institution where he received his early training."

In his last years at Columbia, Professor Smith's health was evidently weakening. Handicapped as he was also, during the war, in his task of running a gigantic department with a sadly depleted staff, these difficulties were still further increased by unfortunate controversies, and his final collapse was by no means unexpected. Those who may have formed their opinion of him during this period can have no conception at all of the inherent nobility and sterling character of the true Alexander Smith. His many friends, knowing his real worth, will long cherish him in their memory.

JAMES KENDALL

NEW YORK.

PREFACE TO THE SECOND REVISED EDITION

Advances in theoretical knowledge and improvements in industrial practice during the past ten years have made innumerable changes necessary in this second revised edition. The most significant alterations will be found in the chapters on Chemical Equilibrium, Ionization and Atomic Structure, but the majority of the remaining chapters have also been considerably modified.

It is hoped that the addition of reading references at the end of each chapter will prove of value to the student. Many of these references discuss important recent developments in chemistry in greater detail than is possible in the text itself.

The numerous "pie-diagrams" illustrating the uses of various chemicals have been left unchanged from the last edition, since in most cases the latest available data, referring to the years of depression, would be more misleading than the older figures. Where any really significant changes have occurred, however, special reference is made thereto in the text.

The reduction in size of about 70 pages is mainly illusory, being counter-balanced by the slightly longer page and the increased proportion and closer setting of small-type material.

The author sincerely trusts that, in spite of the extensive recasting which the *Inorganic Chemistry* has suffered owing to the onward march of science, it still merits the title of "a characteristic Smith text." Most older teachers need no reminder of what this implies, but those who did not enjoy the privilege of contemporary contact with Alexander Smith and those to whom his guiding principles are unfamiliar might, after reading through his preface to the first edition of this book, refer to the Journal of Chemical Education, vol. 9, page 255, 1932.

JAMES KENDALL

EDINBURGH.

PREFACE TO THE FIRST EDITION

This book, the first draft of which was written six years ago, is the outgrowth of the introductory course in chemistry which the author has given for the past fifteen years. A subject undergoing the persistent, though unconscious criticism of keen minds should gain in self-consistency and coherence as it is presented year after year. For example, an answer must be found for the common question, "Why does the chemistry of the laboratory differ from the chemistry of the text-book and the lecture to such an extent that they seem to be different sciences?" The chemistry of the laboratory is, of course, the only real chemistry, and that of the lecture must be somewhere at fault. The student neither sees nor weighs atoms, for instance, and so the details of the laboratory experiment, which *are* seen and studied, become the basis of the whole treatment. The atom and the ion assume the rôle of merely figurative aids in the description of the facts. Gradually the conception of chemical equilibrium comes to contribute the major part of the explanation which is essential to the evolution of a *system of chemistry* founded upon experiment.

In the choice and arrangement of the material, several principles have served as guides:

The book is intended primarily for students beginning the study of chemistry in a college, university, or professional school. It is assumed that use of the book goes hand in hand with systematically arranged laboratory work in general chemistry. The first four chapters, for example, contain a discussion of a few typical experiments. They appeal directly to experience derived from the performance and observation of these and other similar experiments in the laboratory and in the class-room. In these chapters some of the features which are characteristic of every chemical phenomenon are sought out, put into words, and illustrated.

No conception is defined, and no generalization or law is developed, until such a point has been reached that applications of the conception and experimental illustrations, later to be related in the law, have *already* been encountered, and there is about to be occasion for further applications and illustrations of the same

things in the chapters immediately succeeding. In these chapters the applications are frequent and explicit. Later, page references in parentheses continue to indicate the recurrence of examples which might otherwise fail to be noticed. It is one thing to come to *know* a principle of the science, and quite another thing to have acquired, by constant repetition of the process, a confirmed *habit of using* the principle on every appropriate occasion. To assist still further in the attainment of this end, an attempt is made in the last six chapters again to mention and illustrate, by way of review, the most important principles of the science.

No conception of principle is given at all, unless, in its most elementary aspects, it can be made clear to a beginner; and unless it is capable of numerous applications in elementary work; and, finally, unless a knowledge of it is of material use in organizing and unifying the result of such elementary work.

An attempt has been made to state the laws and to define the conceptions of the science in terms of experimental facts. The figurative language of hypothesis has been employed only in explanations.

Familiarity with physical conceptions and facts is so indispensable to the chemist that no apology is needed for the rather full treatment which some of them have received.

No two chemists would agree perfectly in regard to the apportionment of space. The processes of chemical industry, and the everyday applications of chemical science, cannot all be mentioned. These fields, and that of mineralogy, can be represented by examples, without the incompleteness of the result being in any way a detriment to a work of a general character. Again, a dense array of descriptive material, unillumined by explanation, is a positive injury to an introductory treatise. All reference to historical matters cannot be omitted, but a logical display of the subject can be achieved with comparatively little of the history. Of all the aspects of the science, the theoretical is thus the one whose treatment is susceptible of least abbreviation.

The principles of chemical equilibrium are (and have been for the past half-century) fully as much required for intelligent consideration of the simplest experiment, as is the theory of combining proportions itself. Important parts of the theories of solutions and of the battery are much more recent, but each is equally indispensable to the understanding of matters which cannot long be withheld from the notice of the beginner. Surely space ought not to be saved by entire omission of essential parts of the chief thing that makes

chemistry at all worthy of a place amongst the sciences. Nor may we attain brevity, no matter how great the temptation, by condensing the passages on theory until they reach the limit of comprehensibility by an expert. Without clear exposition, full illustration, and frequent application, laws and principles simply repel, or worse still, mislead the beginner.

We reach the same conclusion from another view-point. Every student should have access to, and should use, reference books devoted especially to descriptive, industrial, historical, and physical chemistry, and to mineralogy and crystallography — at least one good book in each of these five subjects. With the help of the index, the veriest tyro can find, in a few moments, almost anything he wants in four out of five of these branches. But just the opposite is the case with the theory. Only an expert realizes what information he is in need of, and knows under what titles to look for it. And often even the expert would fail to understand the isolated sentence or paragraph when found. In a large proportion of connections the beginner simply cannot use such a book for rapid reference at all. In many lines, therefore, much may be left to outside reading, but for theory almost no dependence can be placed on reference work in other books.

For the reasons enumerated above, an unusually large proportion of space has been given to theoretical matters. The actual amount of theory is no greater than is usual in books of the same class, but the explanations are often fuller. Even so, the beginner will probably find that some parts form reading as stiff as any he is accustomed to undertake, without complaint, in physics or mathematics. It can only be said that easily read modes of presenting the science of chemistry are apt to delude the beginner into thinking he has mastered the subject, when in reality he has simply been steered clear of the chief difficulties.

The order of topics was determined by many considerations, jointly. For example, in the first week of his work, a student may encounter experiments, in connection with which almost every part of chemical theory might usefully be discussed. But mastery of the theory must necessarily come bit by bit, and the theory is therefore distributed through the book. Instead of being introduced as soon as a fragment offers a chance for explanation, the treatment of each of the various theoretical subjects, as far as possible, has been postponed until a whole chapter could be devoted to it. The result makes subsequent reference easier, and facilitates alterations in the

order of study. Thus, the hypothesis of ions is not mentioned as soon as it well might be, because satisfactory treatment of it must follow the molecular and atomic hypotheses of which it is an extension, and because the full explanation of this hypothesis must be preceded by some account of the phenomena of electrolysis and of the essential properties of solutions, and also, by a discussion of chemical equilibrium, a subject which of necessity presupposes two or three months' work in chemistry. There is another disadvantage which arises from a premature explanation of the hypothesis of ionization. When it appears at an early stage, too long an interval separates this subject from the study of the metallic elements, and the details are largely forgotten before the field for their chief employment is reached.

The paragraphs in smaller type are not intended for beginners, but for advanced students and teachers, which accounts for the fact that reference will frequently be found in them to subjects treated systematically in later chapters.

The exercises and problems are simply samples of some of the various kinds of questions which might be raised in dozens at the end of every chapter.

Recent works on general chemistry have been consulted during the revision of the manuscript. Of these A. A. Noyes' admirable *General Principles*, Ostwald's *Grundlinien* — a veritable *tour de force*, and Bloxam's *Chemistry* may be mentioned as having proved most suggestive. The author owes special thanks to several friends who have undertaken the toilsome work of reading part or all of the book in manuscript or in proof, and in particular to his colleagues Messrs. Julius Stieglitz, H. N. McCoy, L. W. Jones, and E. S. Hall, to Dr. J. B. Tingle of Johns Hopkins University, to Mr. C. M. Wirick of the R. T. Crane High School, Chicago, and to Mr. Maurice Pincoffs of Chicago. The author alone is responsible for any defects which may be inherent in the plan of the book and for errors which may have escaped detection, but must gratefully acknowledge the very great benefit the book has derived from the friendly criticism of these gentlemen. Other corrections or suggestions will be gladly received by the author.

ALEXANDER SMITH

CHICAGO, *January*, 1906

CHAPTER

ILLUSTRATIONS

The rise of Michael Faraday from "a bright-eyed errand-boy who slid along the London pavements, with a packet of newspapers under his arm" to the recognized leader of scientific research in Great Britain is one of the great romances of chemistry. Faraday's own account of how he got his start is reproduced in somewhat condensed form below: "When I was a bookseller's apprentice, I was very fond of experiment and very adverse to trade. It happened that a gentleman took me to hear some of Sir H. Davy's lectures. I took notes, and afterwards wrote them out more fairly in a quarto volume.

"My desire to escape from trade, which I thought vicious and selfish, and to enter the service of Science, which I imagined made its pursuers amiable and liberal, induced me at last to take the bold and simple step of writing to Sir H. Davy, expressing my wishes; at the same time, I sent the notes I had taken of his lectures. Early in 1813 he requested to see me, and told me of the situation of assistant in the laboratory of the Royal Institution, then just vacant."

Now let us hear the other side of the story, as told by one Dr. Gassiot: On one occasion Sir H. Davy, showing Pepys a letter, said, "Pepys, what am I to do? Here is a letter from a young man named Faraday; he has been attending my lectures, and wants me to give him employment at the Royal Institution—what can I do?" "Do?" replied Pepys, "put him to washing bottles; if he is good for anything he will do it directly; if he refuses, he is good for nothing."

Faraday showed later that he was "good for" the discovery of benzene and the foundation of the laws of electrochemistry, to mention only two of his important scientific achievements.

The picture (from a painting by Alexander Blaikley) represents Faraday giving the first of a course of Juvenile Lectures, on "Metals," on December 27, 1855. The Prince Consort is in the chair, and his sons, the Prince of Wales (afterwards King Edward VII) and Prince Alfred (the Duke of Edinburgh), are on either side of him.

Faraday was most impressed by the keenness of the school boys and school girls who attended these lectures. As soon as he had finished, they came rushing up to his table to ask questions and to see the experiments. "Those who like it best come first, and they so crowd round the lecture table as to shut out the others."

Mendelejeff was born in 1834 at Tobolsk in Siberia, where his father was director of a school. He was the youngest of a very large family—variously estimated as containing from eleven to seventeen children. His father became blind soon after his birth, and it was only after heroic struggles on the part of his mother that he was

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CHAPTER I

THE CHEMICAL VIEW OF MATTER

The main purpose of science is the tying of facts into bundles.

THOMAS HOBBES.

Human knowledge has become, in recent times, so extensive and complex that the truths ascertained have had to be divided, more or less arbitrarily, into groups. Thus, the study of animals, their classification by structure, life-history, distribution, and so forth, form the group known as zoölogy. Such a group is called a **science,** and includes a more or less *distinct* body of knowledge. There is a widely spread impression that a *science,* like chemistry, is a part of the natural order of the Universe. It is thought that we are trying to find the boundaries of chemistry, as they have been predetermined by nature, and to discover the facts, relations of facts, and laws which nature has provided as a means of classifying the content of the science. Now, the situation is precisely the reverse of this. Nature provides only the materials and the phenomena, and *man* is attempting to classify them. He divides the whole into groups, such as physics, chemistry, botany, etc. Then he classifies the facts within each group, in order that he may more easily remember them and perceive their relations. He often finds that, when new facts are discovered, parts of the classification have to be changed.

That the boundaries of these groups are purely arbitrary, however, and do not exist in the subject-matter itself, is seen at once in our own treatment of them. Thus, for convenience, we take the structure of animals *by itself* and style it anatomy; but we include in the science of physiology the study of the way in which the parts *of both plants and animals* perform their functions; and we assemble cognate parts of two groups in sciences like astro-physics and physical chemistry. The sciences, therefore, are not mutually exclusive, and their boundaries overlap in every direction.

The difficulty in deciding what are the most convenient boundaries

is as great with chemistry as with other groups. At the one extreme we have the **abstract sciences,** logic and mathematics. At the other extreme lie the **concrete sciences** like geology, zoölogy, and astronomy. The former are not concerned primarily with the study of matter at all, but with that of abstract conceptions. The latter deal with definite aggregates of matter, such as the nature and history of a particular deposit of sulphur and their relation to those of other deposits of sulphur, or the structure and history of a particular collection of organic material known as a trout, and their relation to the structure and history of a mass of similar material called a salmon. Between these two sets of sciences are the regions occupied by the **abstract-concrete sciences,** physics and chemistry. These sciences deal in part with the same portions of matter, but in a more abstract way than do geology or biology. To them, all specimens of pure sulphur are alike, whether they have been formed by volcanic action, or have been deposited by bacteria in an entirely different manner. In particular, the line which divides physics and chemistry from one another is often difficult to draw. It is assumed, however, that the reader is already familiar with the elements of physics, and so, in place of entering upon an academic discussion of the nature of this line, we shall allow its location to emerge as we proceed.

The same principle of grouping is pursued *within* each field. Thus the preparation and properties of chemical compounds is called **descriptive chemistry.** The content of this portion of the subject is in turn divided into **organic** chemistry (dealing with almost all the compounds containing carbon) and **inorganic** chemistry, and the content of each of these is further classified according to a plan involving the consideration of the constituents of each compound. The study of the proportions of the constituents in compounds, of the conditions under which chemical action occurs, and related matters of a more abstract character, are grouped together in **theoretical or physical chemistry,** which is likewise subdivided. Again, the means that have been devised for recognizing the components of mixtures or the constituents of compounds and measuring their quantities form the several branches of **analysis.** The subdivisions of chemistry of this kind are numerous, *e.g.*, industrial chemistry, bio-chemistry, colloid chemistry, radio-active chemistry, and so forth.

The ideal in view in thus classifying the content of a science is to convert it into an **organized body of knowledge.** The various ways used to organize the facts of a science will be presented in detail as

opportunity offers. These ways constitute what is called the **scientific method.**

It is only by following intelligently the way in which the science is manufactured, step by step, out of the raw material furnished by observation and experiment, that the student can gain a sound foundation for more advanced work in the same science, or a mental training broad enough in its tendency to add measurably to his efficiency in every other task. The chief object of useful thought, no matter whether the problem is one of language, history, business, or life, is to organize isolated facts into knowledge, and the means of successfully accomplishing this is the use of the scientific method.

What Chemistry Deals With. — Chemistry is the science which deals with *all* forms of matter. It considers the natural kinds, such as rocks and minerals, as well as materials like fat and flour obtained from animals or plants. It deals also with artificial products like paints or explosives. When we wish information about any specimen or kind of matter, we consult a chemist. Now chemists have worked out a point of view which enables them to attack any problem connected with matter in a systematic manner and to state the results in a clear and simple way. **To learn chemistry,** we must **first strive to acquire this point of view** and **to master the technical language** the chemist uses in stating and discussing his results.

Properties. — Suppose that a piece of **rusty iron** is submitted to the chemist. He at once examines the rust and notes that it is solid, reddish-brown in color and earthy in appearance. He separates some of it from the iron and finds it to be brittle, that is, easily broken and capable of being pulverized in a mortar. He finds that its density is about 4.5, that is to say, 1 cubic centimeter of it weighs about 4.5 grams. On heating some of it in a flame, he finds that it does not melt, and must therefore have a very high point of fusion. These qualities he calls *properties,* and more especially physical properties. Since all specimens of iron-rust show exactly the same properties, he often calls them **specific physical properties,** because they are **properties shown by all specimens of a particular species of matter.**

After removing any rust by filing or scraping, the chemist examines the iron, and finds that a fresh, clean surface of it is almost white and metallic in appearance. The metal is tenacious, so that it can be bent but not easily broken. It is ductile and can therefore be drawn out into wire. The chemist finds that its density

is about 7.8, and that the metal is incapable of being melted in an ordinary flame. In addition, he finds it to be strongly attracted by a magnet, while rust is not attracted.

The chemist, then, studies what he calls the specific physical properties of each material, in order that he may be able to recognize and differentiate various materials.

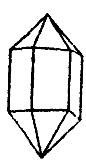
Substances. — All specimens of pure iron show one set of properties, peculiar to iron, and all specimens of iron-rust show a different set, peculiar to rust. The chemist calls **any definite variety of matter, all specimens of which show the same properties, a substance.** Iron is one substance and rust another. A substance is recognized by the specific properties which it exhibits when exposed to various tests.

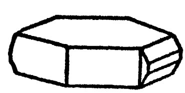
That all bodies of a like kind have identical properties is the first fundamental fact in chemistry. This fact is called the **Law of specific physical properties,** and is stated thus: **The specific physical properties of a substance are constant in all specimens.**

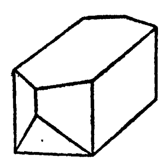
The point of view of the chemist thus consists in describing any material by ascertaining whether it exhibits the properties of one, or of more than one, substance. **He describes it by naming the substances which,** by a study of their properties, **he has found in it.**

The foregoing definition of a substance is very incomplete. Thus, a three per cent solution of common salt in water always has the same properties, yet it is not one substance, but a solution containing several substances. This definition is sufficient for the present purpose, however.

Two Illustrations of the Study and Description of Materials. — If a piece of **granite** is examined by a chemist, he observes at


FIG. 1. Quartz.


FIG. 2. Mica.


FIG. 3. Feldspar.

once that it is spotted in appearance, and made of up several crystalline materials of differing nature. He therefore breaks it up and studies the *properties* of the fragments. Some of the fragments are very hard and are quite transparent, like glass. Larger masses which have exactly the same properties as these fragments are found in nature under the name of *quartz* (Fig. 1). The most

interesting property of this substance is its transparency to ultraviolet light, and although pure quartz is very difficultly fusible, windows of "quartz glass" are now constructed for hospital use in the treatment of rickets. Other fragments from the granite are dark in color and can be split up very easily into shimmering leaves or sheets, thinner than paper. These fragments are identical in all their properties with another substance found in nature called *mica* (Fig. 2). Large sheets of mica are employed, on account of their translucency and infusibility, in furnace windows and lamp-chimneys, and also, because of their insulating value, in electrical machinery. Smaller "spangles" are much used for decorative purposes — for example, to produce a frosted effect on toys and stage scenery. Finally, there are fragments in granite which are neither so transparent nor so hard as quartz and which do not split so easily as mica. These are recognized by the chemist to be identical in their properties with a third substance, *feldspar* (Fig. 3). Feldspar, unlike quartz and mica, melts very easily, and is consequently very largely used as a glaze for china and porcelain. It can be split into layers, but not nearly so easily as can mica. It forms oblong crystals, differing in this also from quartz, which shows hexagonal crystals.* Thus the chemist studies the physical properties of the fragments, and finds that there are three different substances in granite. He reports that the **components** of granite are quartz, mica, and feldspar.

When **flour** is examined by the chemist it appears to the eye to be all alike. Under the microscope, even, all he can learn is that it consists largely of grains, which have the characteristic appearance of grains of starch (see Fig. 175, p. 601). He places some flour on a square piece of cheese-cloth and encloses it by tying with a thread (Fig. 4). On kneading the little bag in a vessel of water, the water becomes milky. When the milky water stands, the white material settles to the bottom, the water can be poured off, and the deposit can be dried. This white substance, when boiled with water, gives an almost clear liquid which jellies on cooling. This is another property of starch. A little tincture of iodine (solution of iodine in alcohol), dropped on a part of the starch, causes the latter to turn blue. This is a very characteristic property of (and therefore *test* for) starch. When the bag of flour is kneaded persistently in water



FIG. 4. Separation of Flour into Starch and Gluten.

* Crystals (see pp. 59–62) are natural forms, of geometrical outline, which solid substances assume. Usually each substance has a distinct form of its own, the particular angles at which the faces meet being peculiar to the substance. Its individual crystalline form is therefore a specific physical property of each substance.

which is frequently changed, the material finally ceases to render the water milky. The starch has all been washed out. When the bag is now opened, a sticky material is found in it. This is called *gluten*. The chemist therefore finds that the flour contains starch and gluten. He learns this by **separating** the two components.

Law of Component Substances. — Every material consists of a single substance, or is a mixture composed of two or more substances, each of which exhibits a definite set of specific physical properties. In terms of these properties the material can be described. This is the second fundamental law of chemistry. This conception was first clearly stated by Lomonossov (1742), a Russian author, statesman, and chemist (1711–1765).

Mixtures and Impurities. — A material containing more than one substance is called a **mixture.** The characteristic of a mixture is that **each of the substances of which it is composed,** although mixed with the others, **possesses exactly the same properties as if it were present alone.** No one of the components affects any other component, or alters any of its properties. Granite and flour are typical mixtures.

The **ingredients of a mixture** are called the **components** (Latin, *componere*, to put together), because they are simply placed together, without change, and can be separated without change.

When a specimen is composed mainly of one substance, and contains only minute amounts of other substances, it is frequently spoken of as a specimen of the main substance containing **impurities.** To be called an impurity, the foreign matter need not be dirty or offensive. Thus, common salt usually contains a little magnesium chloride, a white crystalline solid, as an impurity, and it is this impurity which becomes damp in wet weather. Again, compounds of lime and magnesium are common impurities in drinking water.

Chemically pure (C.P.) means that the quantities of the impurities which the material is apt to contain have been reduced below the amount which would interfere with the most exact chemical work for which the substance is commonly employed. Absolutely pure bodies are unknown.

By convention we frequently speak of *"pure"* hydrochloric acid, or of *"pure"* sulphuric acid, although there may be more than 60 per cent of water present in the former, and 7 per cent in the latter. By this we mean to distinguish the former from "commercial" hydrochloric acid, for example, which contains, in addition to the water, impurities like sulphuric acid and a coloring matter. The water is in fact disregarded, since it is assumed to be present in all cases.

Bodies or Specimens. — It will be seen that *substance* is a general term, like the word "dog," covering the whole species. The *substance* iron includes all the iron in the Universe, and all that was

made in the past or may be made in the future. When we refer to a particular piece of iron, we call it a **body** or a **specimen.**

A **body** is **any particular specimen of matter,** such as a piece of sulphur, a portion of water, a piece of ferrous sulphide (p. 22), a fragment of granite, or some silver nitrate solution. There are thus as many bodies as there are discrete portions of matter. A body may be heterogeneous, or made up of visibly unlike parts, as granite and a **mixture** of iron powder and sulphur are; or it may be homogeneous, or alike in all parts, as are pieces of sulphur and of ferrous sulphide and portions of water and of silver nitrate solution.

List of Important Specific Physical Properties. — We have seen that, to the chemist, knowing the physical properties of all substances is very important. By means of the properties, he recognizes and describes all the bodies he studies. It may be well, therefore, here to give a **list of the more important properties,** most of which have been mentioned in connection with the illustrations we have used.

In the case of **solids,** the chief physical properties the chemist uses are: **color, odor, crystalline form, hardness, solubility or non-solubility** in water and occasionally other liquids, the temperature at which the substance melts (**melting-point**), the **density** (or **specific gravity**), and the **conductivity for electricity.**

In the case of **liquids,** he notes the temperature at which the liquid boils (**boiling-point**), the **density,** the **viscosity,** the **odor,** and the **color.**

Finally, in the case of gases, the properties commonly mentioned are the **color, taste,** and **odor,** the **density,** the **solubility** in water, and the ease or difficulty with which the gas can be **liquefied** (see critical temperature).

It is customary in scientific work to take the weight of 1 c.c. of water at 4° C. and under one atmosphere pressure as the standard (1 gram) to which all density determinations for solids and liquids are referred. On this basis, and on this only, the *specific gravity* of a substance (the ratio of its density to that of the standard) becomes numerically identical with the *density.*

Units of Measurement in Chemical Work. — In chemical work temperatures are invariably measured on the Centigrade scale (see Appendix III). The temperature of a mixture of ice and water under a pressure of one atmosphere is the zero point. The temperature of the steam which rises from water boiling under a pressure of one atmosphere is represented by 100°. The interval between those two points is divided into one hundred equal parts.

For the expression of length, weight, and volume, the metric system is employed. The unit of this system is the meter, which is subdivided into decimeters, centimeters (cm.), and millimeters (mm.). For small measure-

ments the last subdivision is taken as the unit. A cubic centimeter (c.c.) is the unit of volume for small measurements. For larger ones the liter, which contains 1000 cubic centimeters, is used. The unit of weight is the gram. For larger amounts of material the kilogram, which contains 1000 grams (1000 g.), is frequently employed. The meter is equal to about 39⅓ inches in ordinary measures, and the centimeter is very nearly ⅖ of an inch. One liter is about 1/28 of a cubic foot and contains 61 cubic inches. One hundred grams is about 3½ ounces avoirdupois, and one ounce equals 28.35 grams (see Appendix I).

Why do we use the metric system in chemistry? There are several good and sufficient reasons. In the first place, **metric units are international,** whereas in our common weights and measures many chances for confusion exist. Thus the British (Imperial) gallon differs from the U. S. gallon, while the avoirdupois ounce, the fluid ounce, and the troy ounce are all at variance. Science speaks a universal language, and it is essential that the same statement should convey the same meaning to everybody. In the second place, **calculations carried out with metric units are ridiculously simple,** since decimal relationships hold throughout. How much easier it is to convert cubic centimeters to liters than cubic inches to cubic feet, or grams to kilograms than ounces to tons! Thirdly, **metric units are interrelated.** The unit of weight, the gram, is for all practical purposes (*see, however, exercise 18, p. 19*) identical with the weight of the unit volume, one cubic centimeter, of water at the temperature of its maximum density, 4° Centigrade.

Attributes and Conditions. — There are other qualities which a body may possess that we are liable to confuse with the specific properties. Thus, the weight of a piece of sulphur is not a *property* of sulphur. A hundred pieces of as many different substances might all have the same weight, so that a particular weight (say 2 grams) is not a property of any one species of matter. **Weight, dimensions,** and **volume** are **attributes** of a **particular specimen only.** They have different values for different specimens, even when these are all composed of the same substance. The attributes are physical in nature. They are of great importance in chemistry, however, because **they afford the only means we have of measuring quantities of substances.**

There are still other qualities which a body (or specimen of matter) may possess. It has, for example, a certain **temperature, pressure** (state of compression), **motion,** or **electric charge,** and it may be **in solution** in some liquid. A body may change in temperature, pressure, or state of electrification, or it may be dissolved in water, or be recovered by evaporation of the liquid, and yet be the same specimen. A hundred specimens of as many different substances may all have the same temperature — this is not a specific property. These qualities we have just mentioned are all spoken of as **conditions.** The temperature or the pressure of a specimen may be

changed at will. But the specific properties of a substance **under any given conditions** cannot be changed, so long as we have to do with the same substance.

The exact numerical values for many of the specific physical properties of a given substance are significantly altered by a change in the conditions under which the measurements are made, although the substance itself must be considered unchanged. It is consequently necessary to define rigorously the conditions to which any particular values refer. Thus the density of a substance changes with the temperature, and we must define the density as the weight of 1 c.c. at 4° C., or some other *temperature*. We must mention also the *pressure*, particularly in the case of gases, and even in the cases of liquids and solids if it differs from one atmosphere. Again, the melting-point is the *temperature* at which the substance melts at one atmosphere *pressure*. Thus, the **conditions are used also in defining the specific physical properties.**

When the word "properties" is used in speaking of a substance, we always refer to the specific properties only, for a substance is by definition the bearer of nothing but constant, that is, unchangeable qualities. The weight and volume, the temperature and pressure, are variable, and they do not enter into the conception of the substance. This distinction sets the abstract nature of the "substance" in high relief.

The Rusting of Metals. — If we return once more to the subject of rusty iron, we find another point which interests the chemist. If the iron is kept moist — for example, by lying in the grass or partly immersed in water — the layer of rust gradually becomes thicker, and the core of iron becomes thinner until it finally disappears. The rust seems to be *formed from the iron*, in presence of air and moisture. The iron, particle by particle, loses the properties of iron and simultaneously acquires those of rust. Now, **the chemist is concerned,** not only with recognizing substances, but **also with the ways in which substances change and new substances are produced.**

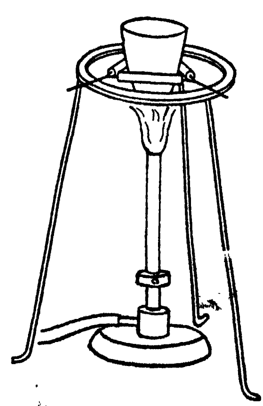


FIG. 5.

Several other familiar metals rust, as does iron, but the change is slower. Thus, lead rusts (tarnishes) slowly, and zinc still more slowly. The change can be hastened by heating. For example, if some lead is melted in a porcelain crucible (Fig. 5), a yellow powder collects on the surface. Gradually more and more of the powder is formed and less and less of the metallic lead remains, until at last

all the metal is gone. Melted tin, when treated in the same way, gives a white powder.

Explanation of Rusting. — The first fact which seemed to throw light on the subject was discovered by a French physician, Jean Rey (1630), who found that the rusts of tin and lead, made by heating and stirring, were *heavier* than the original pieces of metal. He inferred, correctly, that the additional material which caused the increase in weight came from the air. He imagined, however, that the rust was not a new substance, but a sort of froth, and therefore a mixture of air with the metal. Other investigators, such as Hooke (1635–1703) and particularly Mayow (1643–1679), in England, explained the increase in weight by supposing that some material from the air had *combined with* the metal. In other words, iron, for example, was one substance composed of iron only, and rust was another substance, made by union of iron and a material from the air, and not a mere mixture.

It was Lomonossov (1756) who first proved by an experiment that the extra material did come from the air. He placed some tin in a flask, sealed up the mouth of the vessel, and weighed the whole. The flask was then heated and the tin was converted into the white powder. So long as the flask remained sealed, no change in weight was found to have occurred. When the mouth of the flask was opened, however, some air rushed in, and the total weight was then found to be greater. Evidently, during the heating, a portion of the original air had forsaken the gaseous condition and joined itself to the tin to form the powder. This left a partial vacuum in the flask, and more air entered when the latter was opened. Eighteen years later the same experiment was made by Lavoisier, who drew the same conclusion. The rusting of other metals was found to be due to the same cause. Lavoisier named the gas, taken from the air, **oxygen.**

The conclusion can be confirmed in various ways. For example, when the air is pumped out of the flask before it is sealed, the metal can be heated in the vacuum indefinitely without rusting.

A rough imitation of the rusting of iron may be shown to be accompanied by an increase in weight. Iron powder is suspended by means of a magnet over one pan of a balance, and the equipoise is restored by placing small shot on the other pan. When the iron is heated, union with oxygen begins and, after a time, the pointer inclines markedly to one side. The product here is magnetic oxide of iron, however, and not rust (see p. 95).

Experiment to Show the Nature of Rusting. — That a part of the air is consumed when iron rusts is easily proved. We moisten the interior of a test-tube and sprinkle some powdered iron so that it covers and adheres to the whole interior surface. We then set the tube mouth downwards in a dish of water. At first, the pressure of the water compresses the air in the tube very slightly, and the water ascends above the mouth to the extent of a small fraction of an inch only. As the moist iron slowly rusts, however, the oxygen is gradually removed, and the pressure of the atmosphere outside slowly pushes the water farther up the tube. After an hour or more, the water has ascended about one-fifth of the total distance towards the top of the tube (Fig. 6). However long we watch the experiment, and however great an excess of iron we use, the water ascends no farther, while if we make a careful examination of the residual gas in the tube, we find that it exhibits none of the properties of oxygen. Evidently that portion of the air which consists of oxygen has forsaken the gaseous condition, and the water has been forced up to take its place. Inspection of the powder in the tube now shows some reddish particles, where rusting has occurred. The rust, then, is made up of a part of the iron and all of the oxygen that the tube contained.

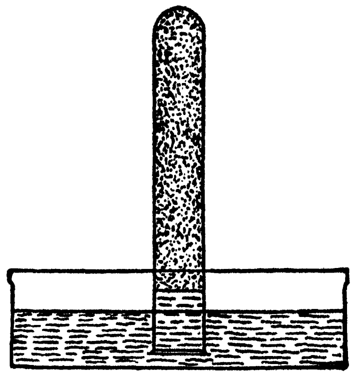


FIG. 6. Rusting of Iron.

Of course, much of the iron powder is unchanged in color, and has not rusted. The air in the tube did not contain oxygen enough to combine with all the iron. The iron that remains is as little able to rust in the remaining gas as in a vacuum.

Incidentally we may infer from this experiment (see, however, p. 454) that atmospheric air is a **mixture,** containing about one-fifth (20 per cent) oxygen by volume. The remaining four-fifths is almost all **nitrogen** (79 per cent), a substance which combines with very few materials, while the balance (1 per cent) is made up of argon and other gases which do not enter into combination with any known substance. If lead, tin, or zinc had been heated in an enclosed volume of air, they likewise would have taken out the 20 per cent of oxygen and would have left the other gases.

An Older View: Phlogiston. — Simple and satisfactory as this explanation appears to us, it must be said that it gained little sym-

pathy from the contemporaries of Rey, Hooke, and Mayow. The other investigators had been prejudiced by a remarkable hypothesis which was supposed to explain both rusting and combustion. Starting with a suggestion by Plato, that during combustion some material escaped from the burning body, and that the flames and heat represented the vigor with which this substance rushed out, Stahl and Becher invented the idea that a substance, which they called "phlogiston," was contained in all materials capable of rusting or burning. Its escape accounted for the phenomena of combustion, and its absence for the alteration in properties of the residual substance. They were perfectly aware that the material was heavier after rusting than before, but refused to sacrifice their hypothesis to a mere fact like this. So they ingeniously appended the suggestion that phlogiston was a substance which not only was not subject to gravitation, but possessed the opposite property of levity! Thus, its escape rendered the material from which it issued heavier than before! Instead of demanding the preparation and examination of phlogiston itself, and the demonstration that it weighed less than nothing, the generality of chemists of that age accepted the idea without proof. It is not surprising, therefore, that many of their attempts to explain chemical experiments on the basis of an assumption which was the precise opposite of the truth should have resulted in hopeless confusion. The fact that foreign matter was actually gained by a body during the process of rusting was not generally accepted until it was demonstrated anew by Lavoisier in 1774 (p. 12). The whole development of chemistry was stunted by the general belief in the conception of phlogiston and, during the one hundred and fifty years which passed between the work of Jean Rey and his contemporaries, and that of Lavoisier, relatively little progress was made.

The introduction of the balance into the chemical laboratory, and the first use of measurements of weight as a means of exploring and explaining chemical changes, is frequently ascribed to Lavoisier. As a matter of fact, it is difficult to state when measurement of weight first became the chief ally of the chemist in his work. Important and conclusive results were obtained by its means, however, before the time of Lavoisier, for example, by Jean Rey, Boyle, Lomonossov, and Black (1728-1799).

The Law of Chemical Change. — The examples of rusting cited in the preceding paragraphs show that specimens of matter can lose their original properties and acquire new ones. Since a substance is "a species of matter, with a constant set of properties," we are

compelled to decide that, when a material *changes* its properties, it has, in doing so, become a *new* substance. This consideration calls to our attention the **third** of the fundamental **laws of chemistry,** namely, that **the material forming one or more substances** (such as oxygen and iron), without ceasing to exist, **may be changed into one or more entirely different substances.** Such a chânge is called a **chemical change,** or **reaction.**

In chemistry, **conditions** are often altered in order to bring about, or to stop, chemical change, or to modify the speed with which it takes place. Thus, we heated the lead (raised its *temperature*) in order to hasten the process of rusting. If a substance, or mixture, is capable of undergoing ordinary chemical change, then the change is always hastened by raising the temperature, and is always delayed or prevented by lowering the temperature. Similarly, changing the pressure in a gas, or dissolving a substance in some liquid, frequently hastens or delays a chemical change in which the substance takes part. The proper physical conditions are, therefore, considered in connection with every chemical operation. **Conditions are used to produce, modify, or control chemical change.**

The commoner kinds of chemical reactions may be divided, for convenience, into four varieties. We can now define the first of these.

First Variety of Chemical Change: Combination. — In each case of rusting, two substances (a gas and a metal) came together to form a third substance (an earthy powder). Apparently two substances may come together in two different ways. They may form a mixture, in which both substances are present and retain their properties, or they may react to form a single substance with different properties. When **two (or more) substances unite to form one substance,** the change is called chemical **combination** or **union.** The product is called a **compound substance.**

We are very careful never to speak of a compound substance as a mixture. Rust is not a mixture of iron and oxygen; it shows none of the properties of either. Nor do we call a mixture (like granite) a compound, or the operation of mixing, combination or union. These are technical words in chemistry and, to avoid confusion, may be used only with due regard to their technical meanings.

Constituents. — As we have seen, we speak of the substances in a mixture as the components. When we wish to refer to the forms of matter which are chemically united in a compound, we call them

the **constituents** (Latin, *constituere,* to stand together) of the compound substance. Thus, iron and oxygen are the constituents of rust.

The chemist **separates** (p. 8) the components of a mixture, for that is all that is necessary. He **liberates** the constituents of a compound, however, because *they* are bound together in chemical combination.

The names given to compounds are usually devised so as to indicate the nature of the constituents. Thus, iron-rust is oxide of iron (or ferric oxide, from Latin, *ferrum,* iron). The yellowish powder from lead is lead oxide or oxide of lead, and the white powder from tin is oxide of tin.

A Condensed Form of Statement. — We may represent a chemical combination, or indeed any kind of chemical change, in a condensed form, thus:

$$\text{Iron} + \text{Oxygen} \rightarrow \text{Oxide of iron (ferric oxide).}$$

Each name stands for a substance. Two substances in contact with one another (mixed), but not united chemically, are connected by the + sign. The arrow shows where the chemical change comes in, and the direction of the change. We read the statement thus: Iron and oxygen brought together under suitable conditions undergo chemical change into oxide of iron, called also ferric oxide. Similarly we may write:

$$\text{Lead} + \text{Oxygen} \rightarrow \text{Oxide of lead.}$$
$$\text{Tin} + \text{Oxygen} \rightarrow \text{Oxide of tin.}$$

The Increase in Weight in Rusting. — As we have seen, the process of rusting is accompanied by a slow increase in the weight of the solid, due to the gradual addition of oxygen to the metal. Now this increase in weight ceases of its own accord, when a certain maximum has been reached. This occurs when the last particles of the metal have disappeared. Thus, the lead gains in weight until every 100 parts of the metal have gained 7.72 parts of oxygen, and the tin until every 100 parts have gained 26.9 parts of oxygen. When these increases have occurred, the metal is found to have been all used up, and prolonged heating and stirring cause no further union with oxygen and no further change in weight. This fact, that each substance limits itself of its own accord to combining with a fixed proportion of the other substance, in forming a given com-

pound, is one of the most striking facts about chemical combination. In mixtures, any proportions chosen by the experimenter may be used. In chemical union, the experimenter has no choice; the proportions are determined by the substances themselves. Thus, 100 parts of iron when turning into ordinary red rust take up 43 parts of oxygen, no more and no less.

This fact enables us to make our condensed statements more specific and complete by including in them the proportions by weight used in the chemical change:

Iron (100) + Oxygen (43) → Ferric oxide (143).
Lead (100) + Oxygen (7.72) → Oxide of lead (107.72).

The following numbers, which represent the *same proportions* by weight, are the ones commonly used by chemists, for reasons which will be given later (Chapter V):

Iron (223.36) + Oxygen (96) → Ferric oxide (319.36).
Lead (414.4) + Oxygen (32) → Oxide of lead (446.4).

A Word of Warning. — A student who has already obtained in a previous course a clear understanding of atomic and molecular weights, and of their utilization in the writing of formulæ and equations, should be encouraged to exercise his skill by re-writing the condensed statements given above, and those which he will encounter in succeeding sections, in their final chemical form. The figures (other than percentages) added in brackets to these condensed statements are furnished, in point of fact, for the express purpose of assisting such a student. In general, however, it is highly inadvisable to rush a beginner too rapidly through the introductory stages of the science. The statement that the learner wants to employ the tools of his trade as early as possible sounds plausible, but any one who handles tools without a proper appreciation of their use is liable either to cut himself or to injure the tools. The beginner who writes equations without understanding their significance is almost certain, indeed, to write them incorrectly, and will tend by force of habit to continue to write them incorrectly even after he has been taught the principles upon which they should be based. Furthermore, the very fact that he has been using formulæ prior to a study of atomic and molecular weights is apt to minimize, in his view, the importance of these fundamental conceptions. Why (he feels) should he be forced to follow every step of the rather involved reasoning by which molecular formulæ are derived and justified, when he has been employing these same formulæ all along without having to bother about theory? If chemistry is to be taught as a logical science, not as a multitude of disconnected facts, *some* theoretical development of atomic and molecular weights *must precede* the practical application of these principles in deducing formulæ and making complete equations.

Summary. — Thus far, we have learned that chemistry deals with substances and their physical properties, and with the changes

which substances undergo. We have discussed and defined a number of important words expressing fundamental chemical ideas. Finally, we have touched upon the weights of the materials used in chemical change, a subject of great importance which will be more fully developed in a subsequent chapter.

Exercises. — 1. Take one by one the words or phrases printed in black type and the titles of the sections in this chapter, and endeavor to recollect what you have read about each. In each case try, (*a*) to recall the meaning and to state it in your own words; (*b*) to recall the facts associated with, and the reasoning which lead up to, the point in question; (*c*) to recall examples illustrating the conception and to apply the conception in detail to each example. Whenever memory fails to give a perfectly clear report of the matter in hand, the text must be read and re-read until the essential point can be repeated from memory.

Use the same method in all future chapters. A useful practice is to employ a pencil as you read and to underline systematically all the important facts and statements, and then to go back and apply to each marked place the process described above.

2. Define the following terms: Specific gravity, tenacity, melting-point, specific physical property, pure body, vacuum.

3. Is it logical to say "pure substance"?

4. Why do we decide that granite is a mixture and iron a single substance?

5. Do the statements in the text prove conclusively that air is a mixture and not a compound (see p. 454)?

6. What weight of oxygen would be required to convert 25 grams of lead into oxide of lead?

7. Make a list of the technical words we have defined, and place the definition opposite to each.

8. What weight of tin would be contained in 15 grams of oxide of tin?

9. If any of the following are mixtures, mention the facts which show them to contain more than one substance: (*a*) muddy water, (*b*) an egg, (*c*) milk.

10. In recognizing a specimen to be quartz, does the chemist consider (*a*) the weight, (*b*) the temperature, (*c*) the length of the specimen? If not, why not?

11. Give a list of the specific properties mentioned in this chapter.

12. What is the increase in volume when 100 g. of iron rust completely (pp. 5–6)

13. If 5 grams of tin and 4 grams of oxygen were heated together, which of the two would remain in part unused? How much of this would remain (p. 16)?

14. Is the form of a cut diamond (p. 559) a specific property or an attribute?

15. Is the form of a cube of table sugar a specific property or an attribute? Is the form of one of the small crystals comprising this cube a specific property or an attribute?

16. The following are popular definitions of the pint: (*a*) A pint of pure water weighs a pound and a quarter (Great Britain); (*b*) A pint weighs a pound all the world round (U. S.). Use these definitions to express the British and the U. S. quarts in metric units, and compare your results with those given in Appendix I.

17. The meter was originally defined as one-tenmillionth of the earth's quadrant from the equator to the pole through Paris. Suggest reasons why this did not prove to be a practical standard. The present accepted value of the mean polar quadrant is 6563.3 miles. What is the difference between this and 10 million meters?

18. The kilogram was originally designed to have *exactly* the same mass as that of a cubic decimeter of pure water at the temperature of its maximum density. It was soon discovered, however, that the standard kilogram that had been obtained by experiment on this basis was not quite accurate. The *present* accepted experimental relation is that 1 kg. of water at 4° C. and 760 mm. pressure measures 1000.027 c.c. Which, in your opinion, is the better procedure: to abandon a rigid simple relationship between the metric units of mass and of length, or to change one of these units every time more careful measurements are made? Give reasons for your answer, and discuss with your instructor.

19. At what temperature Centigrade would the Fahrenheit reading be zero? At what temperature would the Fahrenheit and Centigrade readings be the same? At what temperature would they be the same numerically, but opposite in sign?

20. Historically, the Fahrenheit zero was supposed to represent the lowest temperature obtainable with an ice-salt freezing mixture. We know now that this temperature is —21.2° Centigrade. What is this on the Fahrenheit scale?

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* The *Alembic Club Reprints* (obtained from Oliver and Boyd, Tweeddale Court, Edinburgh, for 65 cents each, post-free) reproduce the original publications of great chemists in accessible form and should prove of considerable value in furnishing the student with a historical background. For a description of the Alembic Club, reference should be made to Dobbin, Journal of Chemical Education, 6, 1225, 1929.

CHAPTER II

CHEMICAL CHANGE AND THE METHODS OF STUDYING IT

We must now take up some new examples of chemical change. They will aid us in introducing one or two additional conceptions and laws. These are continually used by the chemist, and without them we cannot begin the systematic study of the science.

Another Case of Combination: Iron and Sulphur. — Since oxygen is an invisible gas, there is a slight difficulty in realizing that rusting consists in the union of *two* substances—this gas and a metal. The present example is less interesting historically, but it is simpler because both substances are visible and are easily handled. The case of iron and sulphur will enable us to illustrate the same point of view and to practise the application of the same technical words. It will also introduce us to two manipulations—filtration and evaporation—which are frequently used by the chemist.

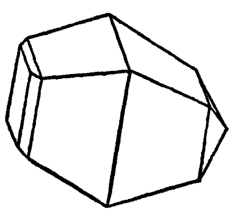


FIG. 7. Rhombic Sulphur.

We begin by observing the physical properties of the two substances. Those of **iron** have already been noted (p. 5).* **Sulphur** is a pale-yellow substance of low specific gravity (sp. gr. 2). It is easily melted (m.-p. 114.5° C.). It does not dissolve in water — that is, it does not mix completely with and disappear in water, as sugar does on stirring. It does dissolve readily in certain other liquids, such as carbon disulphide, however. It crystallizes in rhombic forms (Fig. 7). It is not attracted by a magnet.

* References to previous pages are used in order to save needless repetition in writing. The beginner requires endless repetition in his reading, however, and must *form the habit* of examining, in conjunction with the current text, the parts referred to. The passages cited are, by the reference, *made part of the current text*, which will usually not be clear without them. The same remark applies to topics referred to by name. Such topics must be sought in the index.

All terms, and especially those borrowed from physics, if not perfectly familiar, must be looked up in a work on physics or in a dictionary.

Study of the Mixture, before Combination. — Now, if some iron filings and pulverized sulphur are stirred together in a mortar, the result is a *mixture.* True, the color is not that of either substance, but with a lens particles of both substances can be seen. Passing a magnet over the mixture will easily remove a part of the iron, and with the help of a lens and a needle the mixture can be picked apart particle by particle, completely. We can **separate** the *components* of the mixture more expeditiously, however, **by using** manipulations based upon certain **suitable properties.** Thus, sulphur dissolves in carbon disulphide while iron does not. If, therefore, a part of the mixture is placed in a dry test-tube along with some carbon disulphide and is shaken, the liquid dissolves the sulphur and leaves the iron. To complete the separation, the iron must be removed from the liquid by filtration, and the sulphur recovered by evaporation of the carbon disulphide.

Filtration. — Iron, or any solid, when it is mixed with a liquid or with a solution (like the solution of sulphur in carbon disulphide) is said to be **suspended** in the liquid. If the solid is one that settles rapidly, the liquid may be separated from the solid, in a rough way, by pouring off as much of the clear, supernatant liquid as possible. This is called **decantation.**

A complete separation is effected by pouring the mixture on to a cone of filter paper supported in a glass funnel (Fig. 8). The liquid, together with anything that may be dissolved in it, runs through the pores of the paper and down the hollow stem of the funnel. The liquid is then called the **filtrate.** The particles of the suspended solid are too large to pass through the pores, and so collect on the surface of the filter paper. This operation, like everything the chemist does, takes advantage of differences in the physical properties of the various materials.

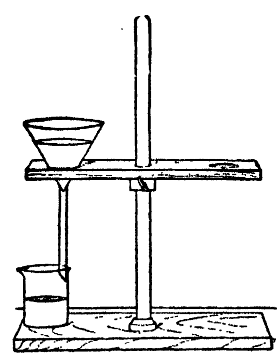


FIG. 8. Filtration.

The material remaining on the paper (the **residue**), when dry, is wholly attracted by a magnet and shows all the other properties of iron.

Evaporation. — To recover the sulphur, the solution in carbon disulphide — the filtrate — is poured into a porcelain evaporating

dish. (Carbon disulphide is very inflammable. Keep flames away!) When the vessel is set aside, the liquid gradually passes off in vapor (e-vapor-ates). Sulphur, however, does not evaporate at room temperature and remains as a **residue,** in the form of crystals of rhombic outline, in the bottom of the dish (Fig. 9). Here, again, differences in physical properties have been utilized.

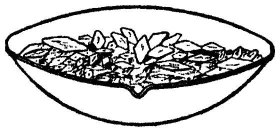


FIG. 9. Evaporation.

Since the physical properties of two substances are not changed by mixing, we have thus used the properties of the iron and sulphur so as to separate them once more. The iron is on the paper; the sulphur is in the dish.

Combination of Iron and Sulphur. — But iron and sulphur are capable of **combining** to form an entirely new substance, if we alter the conditions by raising the temperature. When we place some of the original mixture of iron and sulphur into a clean test-tube and warm it, we soon notice a rather violent development of heat taking place, the contents begin to glow, and what appears to be a form of combustion spreads through the mass. The heating employed at the start falls far short of accounting for the much greater heat produced. When these phenomena have ceased, and the test-tube has been allowed to cool, we find that it now contains a somewhat porous-looking, black solid. This material is brittle; it is not magnetic; it does not dissolve in carbon disulphide; and close examination, even under a microscope, does not reveal the presence of different kinds of matter. This substance is known to chemists as **ferrous sulphide** and, as we see, its properties are entirely different from those of its constituents.

In this connection we must not omit to notice that, as in rusting, a certain fixed proportion will be used in forming the compound. We find that, for 100 parts of iron, 57.4 parts by weight of sulphur are required. If more iron is put into the original mixture, then some unused iron will be found in the mass after the action. If too much sulphur is employed, some may be driven off as vapor by the heat and any that remains, beyond the correct proportion, can be dissolved out of the ferrous sulphide with carbon disulphide. The sulphur which has combined with the iron, however, is no longer present as sulphur — it has no longer the properties of sulphur, and therefore cannot be dissolved out. The chemical proportions are:

Iron (55.84) + Sulphur (32.06) → Ferrous sulphide (87.90).

Another Illustration: Mercuric Oxide. — It has already been demonstrated (p. 13) that air contains an active and an inactive gas. A pure specimen of the *active* gas (later to be named oxygen) was first obtained in 1774 by Priestley from mercuric oxide, a bright red, rather heavy powder. When this substance is heated in a test-tube, we find that a gas is given off. This gas is easily shown to be different from air, since a glowing splinter of wood is instantly re-lighted on being immersed in it. The gas is pure **oxygen.** During the heating, we notice also that a metallic coating appears on the sides of the tube, in the form of a sort of mirror. Apparently the vapor of some metal is coming off with the oxygen and condensing on the cool parts of the tube. As this shining substance accumulates it takes the form of globules, which may be scraped together. It is, in fact, the metal **mercury,** or quicksilver. If the heating continues long enough, the whole of the red powder eventually disappears, and is converted into these two products.

The extensive nature of the change in properties in this case is evident. It should also be observed that continuous heating is required to maintain this change in operation. It differs markedly from the iron and sulphur case in this respect. When the flame is removed, the evolution of oxygen ceases. The significance of this will appear later (p. 253).

Second Variety of Chemical Change: Decomposition. — Priestley's experiment introduces to us a second and very common kind of chemical action. The first variety was combination or union (p. 15). The **second** is called **decomposition.** It consists in starting with a **single substance** (here mercuric oxide) and **splitting it into two (or more) substances,** which differ in properties from the substance taken and from one another. Here, the red powder gave mercury, a liquid metal, and oxygen, a colorless gas.

Simple and Compound Substances. — If we place before a physicist samples of iron, ferrous sulphide, and sulphur, he will report that there are three absolutely distinct *substances* represented, because they show three different sets of physical properties. A chemist, on the other hand, while admitting the accuracy of the report, in view of the criterion used by the physicist, which indeed he uses himself (compare p. 6), will insist on adding that there are only two perfectly distinct *kinds of matter* in the set, because he can make the second from matter furnished by the other two. The same sharp contrast in the points of view arises when mercury,

mercuric oxide, and oxygen, or any similar set of substances, is submitted to the same two tribunals. In a sense, chemistry reduces the kinds of different matter to a much smaller number than does physics or any of the other sciences, and so it is the final authority in all questions involving matter. By the chemist, dozens of physically distinct substances are regarded as closely related because they all can be made with iron, or when decomposed give it; hundreds are alike in that sulphur enters into their composition; thousands are compounds of oxygen. In fact, the number of kinds of matter which are perfectly distinct in the strictly chemical point of view is quite limited.

The conception contained in the last statement was not reached until centuries of effort had been spent in trying, by chemical reactions, to make gold out of pyrite (a shining yellow mineral), or silver out of lead. The first to put our modern view into definite language was Robert Boyle (1661). Later, and independently, it was stated very clearly by Lavoisier in his *Traité de Chimie* (1789). Lomonossov never believed in phlogiston (p. 14), although all his contemporaries did, and the later investigations of Lavoisier finally overthrew this absurd hypothesis and caused the general acceptance of the view that chemical changes involved only combination or decomposition of different kinds of matter. His work showed, also, that decomposition had its limits. We can decompose mercuric oxide by heat, and we have other ways of decomposing compounds like oxide of tin and ferrous sulphide, but we have never succeeded in decomposing the mercury or the oxygen, the iron or the sulphur themselves. **Substances which we are not able, by the ordinary types of chemical change, to decompose into, or to make by chemical union from, other substances** are called **simple substances or elements. A compound,** on the other hand, **is a substance which can be made by chemical combination of, or can be decomposed into, two or more substances.**

Several substances, regarded in Lavoisier's time as elementary, have since been shown to be compounds. Thus, quicklime was considered to be a simple substance until Davy, in 1808, prepared the metal calcium and showed that quicklime was the oxide of this metal. Hence, we do not say that the substances regarded as simple *cannot* be decomposed, but only that they are substances which we "are not able" (at present) to decompose. We have, nevertheless, as will be seen in subsequent chapters, so developed in recent years our knowledge of that part of chemistry which deals with the ultimate structure of matter that it is quite incon-

ceivable that any such error as was made in the case of quicklime can recur in the future.

The phrase **"by the ordinary types of chemical change"** is very important. Although we are not able to effect any decomposition of the elements by chemical reactions similar to those studied in preceding sections of this chapter, yet we cannot regard them as absolutely unalterable and permanent. The rare element *radium* cannot be decomposed in a chemical reaction, in the sense that mercuric oxide was decomposed (p. 23), but every specimen of radium is undergoing, very gradually, continuous and *spontaneous* "disintegration" into the elements *helium* and *lead* (see p. 468). The phrase "at will" was formerly employed in place of "by the ordinary types of chemical change" in the definition of the term element to care for transformations of this type, which we can neither hasten, retard, nor stop by any variation in conditions, but it was discovered by Rutherford (see p. 484) that certain common elements, such as *nitrogen* and *aluminium,* may be disrupted **at the will of the experimenter** with formation of *hydrogen,* by exposing them to the action of the swiftly-moving helium particles ejected from radium in the course of its disintegration. Such phenomena, however, need not affect our conception of elements as applied to everyday chemical reactions, and for our immediate purposes the definition of the word element given above is sufficient.

Chemistry is progressing so rapidly nowadays that it is impossible to draw up a perfectly hole-proof definition of the term *element.* It has been suggested by Prof. Frederick Soddy, in fact, that a reward of a million pounds sterling for such a definition could safely be offered by the Chemical Society of London, since nobody would ever succeed in claiming it. The definition given above suffers from the defect that what is regarded as very unusual today may be the ordinary experience of tomorrow. Twentieth-century advances in physico-chemical theory, showing that the "atoms" of which elementary substances are composed are made up of different aggregates of positive and negative electrical units, have revived the idea that it must be perfectly feasible to transmute one stable element into another (*e.g.,* mercury into gold) merely by re-arrangement of these electrical units into more or less complex aggregates than the original. Such transmutations — albeit on a very small scale — have actually been brought about in recent years in several ways. For example, the bombardment of atoms of lithium by *protons* (positive electrical units, see p. 472) results in the production of helium, while the bombardment of atoms of nitrogen by *neutrons* (close associations of one positive and one negative electrical unit, see p. 478) involves the formation of both boron and helium. A more logical definition of the term *element,* in view of the above facts, will be presented in a later chapter (p. 502), after our knowledge of atomic structure has been developed in detail.

Elements. — The word element is used in two senses. It is applied to the simple substance. Thus we speak of "the element iron," meaning the metal iron. It is applied also to the iron-matter contained in ferrous sulphide or in ferric oxide. The reader should note that it is correct usage to speak of the *element* iron and the *element* sulphur in ferrous sulphide, but a chemist would never say that this compound contained the *simple substances* iron and sulphur. If he did, we should understand him to mean that it was a mixture, and we should expect parts of the material to be magnetic like iron, and other parts to be yellow and soluble in carbon disulphide, which is not the case. In the same way the *name* of an element (such as "iron") is applied both to the material in combination and to the free substance. Thus "iron" may mean free, uncombined, metallic iron, or iron-matter in some compound. The sense in which the word is employed must be inferred from the context or circumstances. When a chemist speaks, as he sometimes does, colloquially, of "iron" in a drinking water, for example, we know at once that he refers to iron in the form of some compound, for metallic iron does not dissolve in water and, if it did, would quickly turn into rust or some other form of combination.

The word **element,** then, means **one of the simple forms of matter, either free or in combination.**

In formally describing a body or specimen, the chemist always avoids the ambiguity just referred to *by naming the components, i.e.,* the substance or substances it contains. He assumes that the nature and constituents of these substances will be known to anyone hearing or reading the description. If he says the body contains zinc and sulphur, it is understood that the body is a mixture of these simple substances. If it contains these elements in combination, the chemist would report that it was sulphide of zinc.

The chemist's work is, nevertheless, still directed wholly by the thought that the individual element (the matter), after combination, remains present in the compound in some form which is, at least, *quasi*-discrete. The readiness of the element to be released once more under suitable conditions seems to favor this point of view (see also p. 69).

Warnings. — A **substance** (p. 6) must be defined by the constancy of its physical properties, and not by saying that it is "a material of some specified, definite composition." * We know many sets of anywhere from two to a

* In chemistry, the word **composition,** when applied to a substance, refers both to the elements present in the compound and to the proportions by weight in which they are present.

dozen or more substances with the very same composition, yet the members of each set have entirely different physical properties, and often are entirely different in chemical behavior. Thus, red and white phosphorus are both composed entirely of phosphorus, yet differ markedly in physical properties. Again, urea and ammonium cyanate have the same composition, but differ in physical properties and, besides, belong chemically to entirely different classes of substances.

Furthermore, a **substance** must not be defined as "a *portion* of matter," for that is the definition of a body (p. 9). A substance is a *variety* or *species* of matter, and not any one portion or specimen. A crystal of salt is "a portion of matter," and a specimen of the substance, but the phrase "the *substance* salt" covers *all* known and unknown specimens of salt, and even not-yet-existent specimens which may be formed in the future.

Beware of defining a **compound substance** (p. 15) as being "composed of two or more simple *substances*." That is a definition of a mixture, and such a product would show two or more kinds of matter with different properties. A compound substance contains only one substance, and every particle has the same physical properties as every other particle. A compound substance might be defined as "a substance composed of two or more elements." This definition, however, is academic, and gives no clue to how a compound is shown to be such. Chemistry is an experimental subject, and all definitions should be stated in terms of the *experimental method of classifying a given case*, as is done in the definition given above (p. 24).

The Common Elements. — Hundreds of thousands of different compound substances are known but, when they are decomposed, it is found that the number of different *elements* contained in them is not great. As we have already said, dozens of substances contain iron, hundreds contain sulphur, thousands contain oxygen. In fact, by the combination of a limited number of simple substances, such as carbon, hydrogen, and oxygen, in different proportions by weight, an almost unlimited number of different compound substances may be produced.

A list containing almost all of the known elements appears on the inside of the cover, at the end of this book, and includes eighty-six names. Actually, ninety-two elements in all (see p. 475) are regarded as capable of existence but, of these, a large number are rare, and seldom encountered. Only about twenty elements occur in nature in their simple, uncombined condition. Three-fourths of the whole number are found in combination exclusively, and must be liberated by some chemical action.

Taking the atmosphere, all terrestrial waters, and the earth's crust, so far as it has been examined, F. W. Clarke and H. S. Washington have estimated the plentifulness of the various elements. The first twelve, with the quantity of each contained in

one hundred parts of terrestrial matter, and constituting together 99 per cent, are as follows:

Oxygen	49.2	Calcium	3.4	Hydrogen	0.9
Silicon	25.7	Sodium	2.6	Titanium	0.6
Aluminium	7.4	Potassium	2.4	Chlorine	0.2
Iron	4.7	Magnesium	1.9	Phosphorus	0.1

Thus oxygen accounts for nearly one-half of the whole mass (see Fig. 10). Silicon, the oxide of which when pure is quartz and in less pure form constitutes ordinary sand, makes up half of the remainder. Valuable and useful elements, like gold, silver, carbon, sulphur, and mercury, are among the less plentiful which, all taken together, furnish the remaining one per cent.

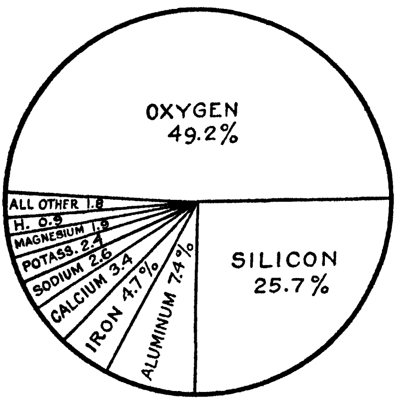


FIG. 10. Composition of the Earth's Crust.

It is convenient in chemistry to divide the elements into two classes — **metals** and **non-metals.** The ordinary distinction of physical appearance (metallic luster) is usually valid; thus iron and copper are typical metals, sulphur and oxygen are typical non-metals. A more exact basis for drawing the line between the two closses, however, will be discussed later (p. 174).

Methods of Work and Observation in Chemistry. — It is not the *end* of chemical work to make generalizations or laws, or conceptions like those dealt with in the preceding paragraphs. These are simply the *means* by the help of which chemical work, whether it be investigation, commercial analysis, or manufacturing, may be carried on more systematically. Together they constitute our system for classifying the facts with a view to ready reference. The sample experiments, if carefully reëxamined, will show that we there employed most of the categories of our classification which have so far been described.

Thus, in the experiment with iron and sulphur (p. 21), it was first our object to find out whether the bodies had interacted chemically on being mixed. To do this we noted the *specific properties* (p. 6) of the substances, separately. Using these properties, we were able

to **identify** the same substances in the mixture, and in this we found no substance with new properties. Part dissolved in carbon disulphide and reappeared after evaporation of the solvent as yellow, rhombic crystals, and the rest was all magnetic. In this connection we purposely omitted all mention of the quantity and temperature, because attributes (p. 10) like the former and conditions (p. 10) like the latter do not characterize substances (since they vary with each specimen), and cannot be used for identification. Coincidence in two or three specific properties is generally sufficient to establish identity.

Most of the properties cannot be recognized readily in *mixtures*, as a moment's thought will show. The general color and the specific gravity of a mixture, containing unknown substances in unknown proportions, for example, tell us little about the corresponding properties of the components. Now, there are few single substances in nature or in the products of experiment, and many mixtures. Hence, **separation** of the components of a mixture usually of necessity precedes the process of identification just referred to. Thus, we first removed the sulphur by dissolving it and then recovered it by evaporation of the solvent, the *boiling-point* of the carbon disulphide (46°) being much lower than that of the sulphur (445°) and its vapor pressure, by virtue of which it evaporated at the temperature of the room, being therefore relatively high. We secured the iron because of its *insolubility*. Those specific properties which can be used for separating mixtures, as well as for identification, are therefore the most important of all. They are the melting-point, solubility, boiling-point, specific gravity, and magnetic qualities, the last being applicable almost exclusively to iron, however.

In connection with this investigation we employed several of the common methods of **manipulation** used by the chemist. These methods are derived from the conceptions described in the last paragraph. Thus we **treated the mixture with a solvent** (p. 21), on the assumption that if it was heterogeneous (p. 9) the components would each behave as if alone present. We then **filtered,** a method invented for dealing with a heterogeneous mixture consisting of a solid and a liquid. **Decantation** is often used in such cases, when the solid is specifically much heavier than the solvent and settles readily. We allowed the carbon disulphide to **evaporate** spontaneously, and this is our favorite method of dealing with a mixture which is homogeneous, and therefore would run through a filter as a whole without suffering separation. When the liquid has a higher boiling-point than 50–60° C., as water has, we use heat from a

steam-bath or Bunsen flame to promote the evaporation. In evaporation we allow the vapor of the liquid to escape, because it is the less volatile, dissolved body that we wish to examine. When we desire, on the contrary, to examine the liquid, the vapor must be condensed. This method, which we have not yet had occasion formally to employ, is called **distillation** (Fig. 11). The jacket round the long tube is filled with a stream of cold water, which, on account

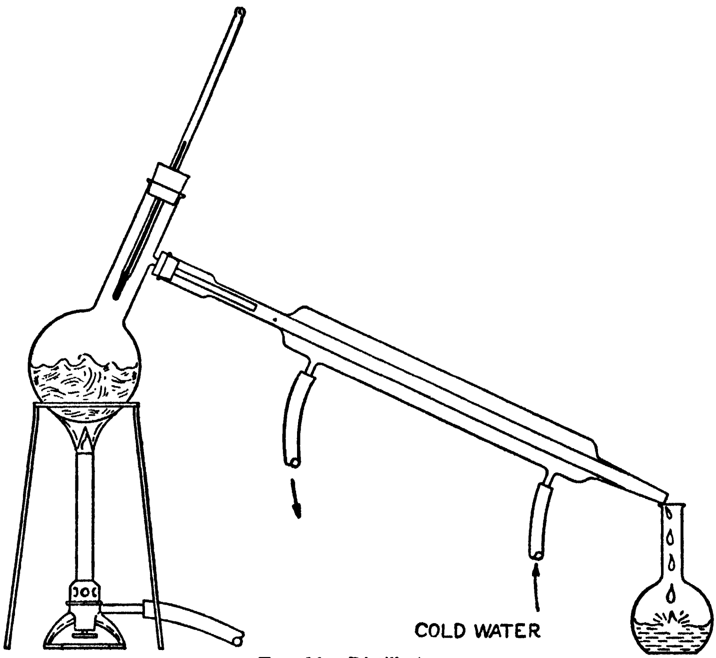


FIG. 11. Distillation.

of its high specific heat, quickly cools and condenses the vapor. The resulting liquid is caught in a flask.

These methods may be adapted to the investigation of any similar problem. Thus, gunpowder is made by the intimate mixing of sulphur, charcoal, and saltpeter (potassium nitrate). If no chemical interaction whatever has occurred, a sample will be wholly separable into these components. If a partial change has taken place, a certain amount of material with different properties will be discovered in the mixture. If the change has been complete, no portion of the original substances will be found. We must first study the specific properties of each of the ingredients separately, in order that a plan

of separation may be devised, and that we may have a basis for comparison with the products of the separation.

It should be noted that our methods of investigating the products of nature and of the laboratory are purposely limited so as not to separate chemically combined, but only physically mixed, forms of matter. After a physical individual has been isolated, and even then only if it has new properties, and is not at once recognized as a known substance, we next proceed to separate it into its chemical constituents so as to learn which elements it contains and in what relative proportions by weight.

The experiment with mercuric oxide simply rang the changes on the same conceptions, and repeated the same manipulations. When we heat the mercuric oxide (p. 23), it is resolved into its constituents. We selected the experiment because the conditions are such that separation of the products from each other and from the original material occurs spontaneously, without further treatment. The separation depends here on the boiling-points of the materials. That of oxygen is very low (—183° C.); so that, being a gas even at ordinary temperatures, it comes off. That of mercury is much higher (357° C.), but the heat produced by the flame (1000°-1200° C. in the bottom of the test-tube) is more than sufficient to vaporize this product also. The speedy condensation on the cooler part of the tube, causing *separation* of the two products, is due to the wide *difference in boiling-points*. The part of the mercuric oxide which is still unchanged, on the other hand, is entirely involatile even at 1200° C.; so that it does not mingle with the vaporized products at all.

A More Complex Chemical Reaction. — The following illustration is taken purposely in order to illustrate the variety of ways in which chemical change may be carried out. It is the interaction of silver nitrate and sodium chloride (common salt) in aqueous solution. The two solid substances may be recognized by the form of the crystals of which they consist. The latter is composed of small cubes (Fig. 12), while the former presents a less familiar form geometrically (Fig. 13). Both substances are capable of being dissolved in water and, for this experiment, portions of each substance are shaken in separate vessels with water, until none of the solid remains. When the solutions are now poured together, we observe that the clear liquids at once become opaque, and that a dense mass of white, solid material appears suspended in the mixture (Fig. 14). This white substance consists of an extremely fine powder without any observ-

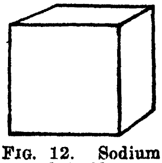


FIG. 12. Sodium Chloride.

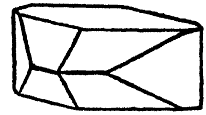


FIG. 13. Silver Nitrate.

able crystalline form. We know at once that it must represent a new substance, since it would not have appeared had it been soluble in water like the two materials from which it was made. We continue adding the one liquid gradually to the other until no further formation of this solid takes place, and then stop. By filtration (Fig. 8), we obtain the insoluble material (the **precipitate**) upon the filter paper, and the clear liquid (the **filtrate**) passes through and is caught in the vessel below.

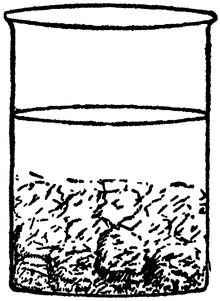


FIG. 14. Precipitation.

We are confronted with two possibilities: either both the original materials have come together to form one white insoluble material, or some other product (or products) may be present in addition to it. In the latter case, search must evidently be made in the liquid. By evaporating the *filtrate* in a suitable vessel (Fig. 9), we find that the second assumption represents the fact, for a considerable quantity of a white crystalline substance remains. The homogeneous character of this shows that there was but one product in solution, while the same property of the precipitate shows that there are but two products altogether.

The insoluble material is composed of silver and chlorine, and it is known as silver chloride. Like some other compounds of silver, it darkens on exposure to light, turning first purple and then brown, and being decomposed by this agency into its constituents. The chlorine, a gas, escapes into the air, and a brown powder consisting of finely divided, metallic silver remains. The soluble solid, obtained from the filtrate, we recognize as identical with a mineral, sodium nitrate, which is found in Chile. Its crystals are rhombohedral (Fig. 22, p. 61). They resemble cubes which have been slightly distorted by pressing inwards two opposite corners. This change presents several features which distinguish it from the previous ones: it is much more complex; it takes place in the presence of water; it requires no heating for its promotion; and the change is complete the instant the materials have been mixed, while the others required a good deal of time for their accomplishment.

The condensed statement for this reaction may be represented as follows, the numbers showing the relative weights as before:

Silver nitrate	+	Sodium chloride	→	Silver chloride	+	Sodium nitrate.
(169.89)		(58.46)		(143.34)		(85.01)

Further discussion of this type of chemical change, which is called **double decomposition,** will be postponed until a later chapter (p. 230).

Fact and Law. — If the preceding pages be reëxamined, it will be seen that a number of **facts** are mentioned in them. We begin the organization of knowledge according to the scientific method by trying to determine the facts. Thus, we find some specimens of iron are variously colored, and some are brittle. Examination shows, however, that the former peculiarities are due to paint, for example, and the latter to the presence of carbon and other foreign materials in the iron (cast iron). Finally, we ascertain the facts that iron itself is silver-white and tough.

Facts are the ultimate units of the structure of a science. Thus, a single isolated observation, no matter how accurately made, does not furnish us with the sort of fact that can receive a permanent place in our collection. It is only after much research and thought that we can ascertain which are the fixed elements in the variety of experience in any line, and so determine what are the facts, in the sense in which we have used the term.

Putting together statements or **laws** like those appearing in heavy type above (pp. 6, 8, 15) is the second step. We examine facts of a like kind, or pertaining to like phenomena, to see whether any general statement can be made that will cover some feature common to the whole of them. For example, after settling the intrinsic properties of several substances, and then determining the facts about the way in which these properties are affected under certain circumstances, we decide that, when one substance gives two entirely different substances, or one of the other varieties of change (p. 15) occurs, the cases in which this takes place shall constitute a distinct class, and we call them cases of chemical change. The statement, which in a few words or phrases sums up those features of all the phenomena of like kind which are constant, is called **a generalization,** or a **law,** or a **principle,** of the science. A **generalization** or **law** in chemistry, therefore, is a **brief statement describing some general fact or constant mode of behavior.** Its uses are to condense a great many similar facts into one statement, and thus to make the whole set of facts more easy to remember.

One section in the first chapter (p. 12) was entitled: **"Explanation of rusting."** If that paragraph be now re-read, it will be found that, in the ordinary (as distinct from the scientific) sense of the word, no explanation was given! It has simply been demonstrated that

when iron rusts it combines with oxygen from the air. This is an additional fact. It shows *how* iron rusts, namely by taking up oxygen, but not *why* it is able to unite with oxygen. We have to go much more deeply than this into the matter before we can claim to know why iron can combine with oxygen gas and platinum cannot.

Explanations in chemistry are of three kinds. (1) We usually try to show that the phenomenon is not an isolated one. Thus, we show that other metals rust. This reconciles us to some extent to the fact that iron rusts, and we feel some mental satisfaction. This is the method of **showing that the fact to be explained is a member of a large class of similar facts.** (2) Next, **we try to get more information about the fact to be explained.** Thus when to the acquaintance with the outward manifestations of rusting, we add the further information that there is an increase in weight, and that this is due to union of oxygen from the air with the iron, we feel increased satisfaction, and say that the fact has been "explained." (3) If we are still dissatisfied, and can discover no further useful facts, **we imagine a state of affairs which, if true, would classify the fact or add to what we know about it.** This step we call explaining by means of a **hypothesis.** We then devote our attention to trying to verify the hypothesis.

Of course, the same set of facts may be viewed in many ways. Picking out the relationships which are most comprehensive and, at the same time, are best fitted to form part of still broader generalizations, or to take their places alongside of equally broad ones, requires the highest ability. The most important laws, like that describing the behavior of gases when compressed (Boyle's law), are usually connected with the names of the men by whom the relationships were discovered and the generalizations formulated.

The reader must beware of the misconception that a law *enforces* behavior in accordance with its tenor. The mere *statement* that every piece of matter attracts every other, cannot compel a stone to fall; nor can the mode of behavior of one falling stone persuade any other to do likewise. The law is simply a record of what is invariably observed to happen.

It is, therefore, also very misleading if we permit ourselves to say that Boyle's law (p. 109) "acts" so as to "cause" gases to behave in a certain way, or that the law "operates" to "produce" a certain behavior, or that other behavior is "impossible" to the gas, or that the law of cohesion "intervenes" when the gas is under low pressure, and causes its behavior to "diverge from that required" by Boyle's law, or to say that a gas "disobeys" Boyle's law. In scientific discussions, such figures of speech are alone permissible as throw light on the subject. Phrases like the above, common as their use is, have been selected apparently with a view to introducing a maximum of distortion and obscurity. It is the gas that "acts" and gives rise to the making of Boyle's law, and the latter is only an epitome of the *way* it acts. The "laws"

of nature are not unchanging, although we are often told that they are. It is the *behavior* in nature that is unchanging. The laws which attempt to describe this behavior are not natural laws, they are man-made. They are continually amended, that they may more closely describe additional facts disclosed by research. Behavior divergent from the "laws of nature" is not only possible, but is constantly being observed. Such divergencies furnish, in fact, the commonest starting points for fresh investigation. Thus Boyle's law was amended by Van der Waals (p. 125), and the law of definite proportions (see p. 478) has been greatly modified recently. It is not the gas which "diverges" from our statement or "disobeys" our law, but our statement which is proved by the behavior of the gas to be inaccurate. Our procedure, in such cases, is always more logical than our language, for we never attempt to cure the gas of its error, but always the law itself by suitable modification in its phraseology.

Physics in Chemistry. — It will be seen that one cannot accomplish anything in chemistry without acquiring and using some knowledge of physics. We measure quantities by means of the physical attributes, weight and volume. We produce chemical change by arranging the physical conditions, for example, by mixing, heating, or using an electric current. Physical means are the only means we possess for producing, stopping, or modifying chemical changes. Again, we ascertain whether a chemical change has taken place or not by observing the physical properties of the materials before and after the experiment. Thus, we noted that the red, powdery oxide of mercury, when heated, gave a liquid metal and a gas. All the phenomena of chemistry are physical. A phenomenon (Greek, φαίνειν, to show) is literally something that is *seen,* or more generally, something that affects any of the senses. Observing physical phenomena is, therefore, our sole means of studying chemical changes. Chemical work is consequently entirely dependent upon the skilful use of physical agencies, and the close observation of physical phenomena for its success.

It is only the inference, following the experiment and the observation, that is strictly chemical. If one substance gives two different substances, or if two substances give one different substance, for example, we infer that a chemical change has occurred. We then try to recognize the substances by their properties and name them.

Changes like that of ice into water, or of water into steam, and *vice versa,* are not regarded as chemical changes. These are called **changes of the state of aggregation.** The solid, liquid, and gaseous forms are different states of the same substance. The very language we use bears testimony to the universal acceptance of the view that change of state does not constitute a fundamental alteration. Thus, we have solid *lead* and molten *lead, air* (the gas), and liquid *air.*

In the case of water alone has it been found convenient to distinguish the three forms, ice, water, and steam, by separate names.

Attempts to Distinguish between Physics and Chemistry.—If the reader has studied elementary chemistry before, he must beware of certain misconceptions which he may have formed in regard to the relation of physics to chemistry. For several reasons, we have omitted most of the usual arguments employed in discussing the difference between chemistry and physics. To discuss the *difference* between two things, when the reader does not yet know anything about one of them (chemistry), and sometimes knows little or nothing about the other, must necessarily be futile. Then, too, the alleged difference between physical and chemical phenomena, as phenomena, does not exist. Heating a platinum wire and allowing it to cool, heating mercuric oxide and decomposing it, and an animal walking, when regarded as phenomena (appeals to the senses) are all physical. The phenomena presented in chemical change, in the structure of plants and animals, in geological formations, and in pure physics are all physical. After we have assigned certain groups of such phenomena to other sciences, what is left belongs to physics as such. But physics still has to be employed in explaining how the limbs of an animal work, how strata are deposited, how the mercury and the oxygen are separated, and how each is recognized in the practical study of chemistry. We cannot omit physics, because it is needed at every turn. Chemistry deals with the interpretation of certain classes of physical phenomena, geology with other classes, and so forth.

Some of the current distinctions between chemical and purely physical phenomena deserve notice. Some physical changes, like the boiling of water and the condensation of the steam, are easily reversible. But no one ever saw a piece of broken glass restored to its original condition. Many toys are broken, and few mended. In fact, some physical changes are easily reversible, and others are not. We shall see later that many chemical changes are also easily reversible, although many are not. There is no distinction along this line. Again, in chemical change, all the physical properties are altered. But, when water is converted into steam or ice, all the physical properties are different. Change in all physical properties occurs in physics also. Still again, the change from iron to rust is abrupt or sharp, while the changes in the properties of iron as it is gradually raised to higher and higher temperatures are gradual. But, when the iron melts, or the water is changed into steam, the change is very sharp. On the other hand, when water is heated from 0° to 100°, chemical changes involving the decomposition of complex into simpler units (see p. 204) undoubtedly occur and, when ammonium chloride vapor is heated, progressive decomposition into ammonia and hydrogen chloride takes place and less ammonium chloride remains, yet no sharp change in properties is noticeable. The absence of abrupt change is due to the fact that the substances in the water and the gases in the vapor are *completely miscible with one another,* so that only gradual change can be noticed. On the other hand, rust and iron, or water and steam, are not miscible, and so two phases are produced. Hence, the change (physical or chemical) is sharp if a new phase is produced but gradual if the products are miscible with the original substances. Finally, it is sometimes said that physical changes are produced by physical or mechanical means, and chemical changes by chemical means. In point of fact chemical changes are produced by mixing substances, or by heat-

ing (producing more violent motion of the molecules), or by using a current of electricity (driving a stream of electrons into a solution), or by other physical and mechanical means, and no other means exist. Practical chemistry consists, therefore, in using physical means to produce and to control chemical change, and to separate and examine the results. Hence, while studying real chemistry, one is bound to use, and to learn much about, practical physics.

Where, then, is the line between chemistry and physics to be drawn? All agree that warm solid phosphorus is chemically identical with cold phosphorus. Nearly all scientific men at present assign the study of the melting and the vaporization of phosphorus and other substances to physics. Some chemists consider the solution of phosphorus in carbon disulphide or some other solvent (it is practically insoluble in water), although the material is recovered unchanged by evaporation of the liquid, as a chemical change. But the great majority regard this as physical also. If not chemically different, the solid, gaseous, and dissolved forms of a substance must be classed as mere physical states of aggregation. On the other hand, red phosphorus is held by most chemists to be chemically different from white phosphorus. Many kinds of matter show as much variety in form as phosphorus, and some show more.

In solving an ordinary puzzle, we work knowing that some simple solution exists When studying nature, we are saved much embarrassment by remembering that, in cases like this, we are not seeking for a clear-cut distinction of whose existence we are assured in advance. Nature is under no obligation to furnish easily classifiable facts at all. The limitations of our minds compel us to classify as far as we are able to do so. On this plan alone can we master the infinity of detail. But the resulting system exists in our own minds, where it originated, and not in nature. In the present instance, we are seeking, as always, to make a distinction for our own convenience. But, at present, the effort to make a final distinction that can be used consistently causes more inconvenience than the alternative of letting the matter rest. The history of previous experiences leads us to hope that, with fuller knowledge we shall be able, sooner or later, to construct a system of classification even for this obscure region. After the distinction has been made and accepted by chemists, and not till then, will it be possible to explain it to students.

Summary. — In this chapter we have learned that, while there are many substances, there is a limited number of entirely different kinds of matter (elements) into which compound substances can be decomposed. We have likewise learned that physical properties are utilized in manipulations, such as filtration and evaporation, as well as for identifying substances, and that physical attributes are used for measuring quantities in chemistry and physical conditions for guiding chemical change. Finally, we have seen that a science is not a natural, but a manufactured, product, and that the science of chemistry is still in the making.

Chemical laboratory work consists largely in the separation, recognition, and description of substances. The importance, especially,

of thorough familiarity with specific properties and the influence of conditions (for example, temperature) to these ends is shown by the examples (pp. 28–32). The system of classification as a whole is part of the everyday mode of thought of the chemist, for thought consists largely in comparing and contrasting, and our system of classification furnishes the plan of this so far as chemistry is concerned. Learning chemistry consists, therefore, in large part in learning this classification and becoming habituated to its use.

The influence of conditions has as yet been barely touched. It will be dealt with more explicitly as occasion offers. The attribute of quantity, which has already received some attention (p. 16), will form the basis of discussion in the next chapter.

It may not be out of place to indicate which are the most important conditions.

The first condition whose influence we are likely to notice in chemical work is that of *temperature*. The accelerating effect of rise in temperature on the speed of all chemical changes (see Chap. VI), and Van't Hoff's law (p. 284) in regard to the effect of temperature on the direction of chemical change, describe the most important characteristics of this influence.

The second condition whose effects we continually observe is that of *concentration*. This, and not chemical affinity, as many suppose, determines chemical behavior in the majority of familiar actions. It is described by the law of molecular concentration (p. 272), or "mass action," as it is often called to the great detriment of clearness. Brin's method of obtaining oxygen furnishes the first conspicuous case of the influence of this condition which we shall encounter. If this and many other examples are passed over without discussion, it is only because we must wait until much chemical experience has been gained before this principle can be understood. *Pressure* is the familiar measure of concentration in gases.

A third condition of great importance in many — perhaps most — chemical actions is the presence of a *catalytic* or *contact agent* (p. 103).

Exercises.* — 1. What physical properties are used (*a*) in filtration, (*b*) in evaporation, (*c*) in the separation and identification of the products from heating mercuric oxide (p. 23)?

2. Describe: (*a*) a red-hot rod of iron, 10 cm. long by 1 cm. diameter, weighing 58.5 g.; (*b*) a solution of 5 g. of sulphur in 20 c.c. (26 g.) of carbon disulphide at 18° C. In doing so, divide the description into attributes, conditions, and properties.

3. Consider the following materials and state whether, so far as you can now judge, each is a single substance or a mixture: (*a*) a candle, (*b*) a cake of soap, (*c*) an egg.

*** The exercises should in all cases be studied with minute care. They not only serve as tests to show that the chapter has been understood, but very frequently also call attention to ideas which might not be acquired from the text alone, or assist in elucidating ideas given in the text which, without the exercises, might not be fully grasped.**

4. What are the two most direct ways of showing a substance to be a compound? Illustrate each?

5. If we say that quicklime contains calcium (p. 24), do we mean the element or the simple substance calcium?

6. What explanation was given, (*a*) of the disappearance of mercuric oxide when heated, (*b*) of the absence of iron and sulphur, as substances, from ferrous sulphide? Which of the three kinds of explanation was used in each case?

7. Take the chemical action on p. 22, par. 3, and enumerate the physical properties of the substances before and after the chemical change.

8. Define the following terms, and find illustrations of each, other than those given on pp. 8 and 16; mixture, physical component, chemical constituent.

9. What (*a*) elements and (*b*) substances are contained in an aqueous solution of sodium nitrate (see p. 76)? Is it correct to say that the simple substance oxygen is contained in it? What then is the difference in meaning between the terms "element oxygen" and the "simple substance oxygen"?

10. Color, volume, melting-point, density, temperature, weight, crystalline form, boiling-point, pressure. In respect to which of these qualities will, (*a*) one substance differ from another, (*b*) one specimen of the same substance differ from another, (*c*) one specimen of the same substance differ at different times? Give the technical names and uses of the sets of qualities which fall under *a*, *b*, and *c*, respectively.

11. What properties are essential in order that two substances may be separated by, (*a*) evaporation, (*b*) filtration, (*c*) distillation?

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CHAPTER III

COMBINING PROPORTIONS BY WEIGHT

If we now return to the illustrations of chemical phenomena which we have been studying (pp. 22, 23, 32), we shall find a new question arising naturally out of them. This is, whether the *mass* of the materials is altered, as are the other attributes, in these chemical changes.

Conservation of Mass. — The most painstaking chemical work seems to show that, if all the substances concerned in the chemical change are weighed before and after the change, there is no evidence of any alteration in the *quantity of matter*. The two weights, representing the sums of the initial factors and of the products respectively, are, indeed, never absolutely identical, but the more careful the work and the more delicate the instrument used in weighing, the more nearly do the values approach identity. We are able to state, therefore, as a law of all chemical phenomena, that: **The mass of a system is not affected by any chemical change within the system.**

This statement simply means that the great law of the conservation of mass holds true in chemistry as it does in physics. Chemical changes, thoroughgoing as they are in respect to all other qualities, do not affect the mass; an element carries with it its weight, entirely unchanged, through the most complicated chemical transformations.

A law, as we have seen (p. 33), is a condensed statement describing some constant mode of behavior. It is simply a summary of our experience. As such, it is subject to modification when a fact is discovered with which it conflicts. Thus, it is perfectly possible that we may yet find cases of demonstrable changes in weight accompanying other physical or chemical changes in a limited system. Indeed, it has more than once been alleged that such changes have been observed. It used to be a law that the earth was flat. It is now more correct to say that a limited area of perfectly level ground is *very nearly* flat.

The same is true with respect to the **law of the conservation of mass.** This principle has no exceptions in everyday chemistry. We can predict with certainty, however, that it must fail for certain reactions at present beyond our power. For example, the man who succeeds in reversing Rutherford's experi-

ments (p. 25), working back from hydrogen to other elements, will find that he can obtain only 4.002 g. of helium from 4.032 g. of hydrogen! What will have happened to the remaining 0.03 g.? We shall have to wait until we reach a later chapter (p. 480) before we are prepared to solve this mystery and *justify the law in an expanded form.*

Superficial observation, as of a growing tree, might seem to give evidence of the very opposite of conservation of matter. But here the carbon dioxide gas in the air, the most important source of nourishment for plants, is overlooked. Similarly the gradual disappearance of a candle by combustion seems to illustrate the destruction of matter. But if we insert sticks of sodium hydroxide in a **U**-tube (Fig. 15) to catch *the gases* which rise through the flame, we find that the gases weigh even more than the part of the candle which has been sacrificed in making them. When we take account of the weight of the oxygen obtained from the air which sustains the combustion, we find that there is really neither loss nor gain in weight. If we carry out chemical changes in closed vessels (Fig. 16), which permit neither escape nor access of material,* we find that the weight does not alter.

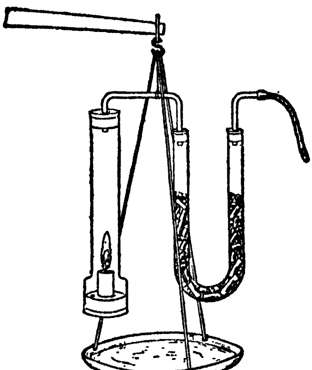


FIG. 15. Conservation of Mass. Burning of a Candle.

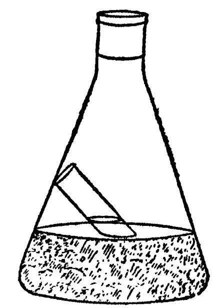


FIG. 16. Conservation of Mass. Precipitation of Lead Chromate.

One way of stating the difference between chemistry and physics is to say that changes in which both the mass and the identity of the substance are conserved belong to the latter, while those in which the mass alone is conserved belong to chemistry.

Law of Definite Proportions. — In the decomposition of mercuric oxide (p. 23) we find that, for every 100 parts of mercury liberated, 7.97 parts of oxygen by weight are set free. Using the

* A test-tube half-filled with a solution of lead nitrate in water is placed inside a tightly-stoppered Erlenmeyer flask containing a solution of potassium dichromate. The whole is placed on one scale of a sensitive balance and carefully counterpoised. The flask is then tilted to allow the two solutions to mix.

numbers commonly employed in chemistry, which represent same proportion by weight, we have the condensed statement,

$$\text{Mercuric oxide } (433.2) \rightarrow \text{Mercury } (401.2) + \text{Oxygen } (32).$$

We find also that mercury and oxygen can be made to combine to form mercuric oxide, and the proportions by weight required are the same. Moreover, every sample of mercuric oxide, whether made by combination, or in any of the other possible ways, always contains this proportion of the two elements. We have already seen that the oxides of lead and tin contain fixed proportions (p. 16) of the metal and oxygen and that ferrous sulphide has a constant composition by weight. The same principle is found to apply to all ordinary chemical compounds, and is stated in the **law of definite or constant proportions: In every sample of any compound substance, formed or decomposed, the proportion by weight of the constituent elements is always the same.**

Another form of statement, which is a corollary of this one, and is applicable more directly to complex chemical actions, is: **The ratio by weight of any one of the factors or products of a chemical change to any other is constant.**

The controversy between Berthollet and Proust, in which the former denied and the latter affirmed the validity of this law, was one of the chief features of the chemical history of the early part of the nineteenth century. The ways of forming or decomposing a compound, or of carrying out a more complex chemical change, may be varied indefinitely. The apparatus, the mode of experiment, and the proportions of the materials may be altered at our will. But, up to 1914, in spite of an enormous amount of careful work, no single case of variation in the proportion of the constituents *actually used* or *produced* in a given chemical action had come to light. If too much of one constituent, for example, is taken, a part simply remains unchanged. A higher temperature may hasten the chemical action, but it does not affect the quantitative composition of the products, provided the resulting substances are of the same nature. It was the work of Stas (1860–65) which settled the question, by proving that even slight variations could not be detected, and disposed of Berthollet's objections. When the composition of a substance seems to be variable, it is usually found on closer examination that mechanical mixtures of some kind were being mistaken for single substances.

A Warning. — Several exceptions to the law of definite proportions, nevertheless, have been discovered during the last twenty years. Thus, ordinary lead chloride (a white salt) contains lead (a metal) and chlorine (a greenish-yellow gas) combined in the proportions 207.2 to 70.92. Richards, of Harvard, however, found that

ead contained in uranium ores gives a chloride in which the portion of lead is as low as 206.1 to 70.92 of chlorine. Again, ddy found that lead extracted from thorium ores gave a chloride containing a proportion of lead *higher* than the ordinary one, namely, 208.4 to 70.92. There thus appear to be three chlorides of lead, having, so far as we know, substantially the same properties, and *being therefore the same substance,* yet differing in composition.

Lead derived from radioactive disintegrations, consequently, enters into compounds, such as lead chloride, in slightly different proportions by weight than does ordinary lead. A very large number of other elements have been shown to exist in two or more forms (*isotopes*), which would, if separable, give compounds possessing essentially the same specific properties yet differing in composition. Only in the case of hydrogen, however, has the separation of isotopes on a large scale so far proved to be practicable, and here, for special reasons (see p. 483), the difference in composition of corresponding compounds *is* accompanied by significant differences in specific properties. Detailed discussion of these points must be deferred to a later chapter (pp. 476–8). For all *practical* purposes, it is most important to note, the law of definite proportions is still universally valid.

Above all things, the beginner must be careful not to get the idea that our scientific laws are just wild guesses which may have to be discarded at any moment, and that consequently he is wasting his time in learning them. Professor R. A. Millikan, the Nobel Prize winner in physics for 1923, has recently observed: "One of the greatest contributions of science to life is the discovery that progress is in general made by the evolutionary process. *There are no revolutions in science.* Einstein does not replace Newton, he merely supplements him. In so far as Newtonian mechanics was a body of experimental facts, it is eternally true. The whole of Newton is incorporated in Einstein. Let the revolutionary reformer ponder well that fact."

Just as Einstein's theory amplifies our knowledge regarding gravitational forces, so recent discoveries in chemistry serve only to confirm our belief in the fundamental validity of the law of definite proportions, re-stated in a more precise form (see p. 478).

The Measurement of Combining Proportions. — In a number of condensed statements we have given the proportions by weight of the materials combining. It is now desirable that we should know how the necessary measurements are made. One or two brief descriptions, diagrammatic rather than accurate, will suffice to show the principles employed.

If we take a weighed quantity of iron in a test-tube and heat it with more than enough sulphur (an **excess** of sulphur), we get free sulphur along with the ferrous sulphide (p. 22), and no free iron survives. We may remove the free sulphur by washing the solid with carbon disulphide. The difference between the weights of the ferrous sulphide and the iron gives the amount of sulphur combined with the known quantity of the latter.

As an example of the study of the combination of a metal with oxygen, we may weigh a small amount of copper in the form of powder in a porcelain boat and pass oxygen over the heated metal until it is completely converted into black cupric oxide (Fig. 17).

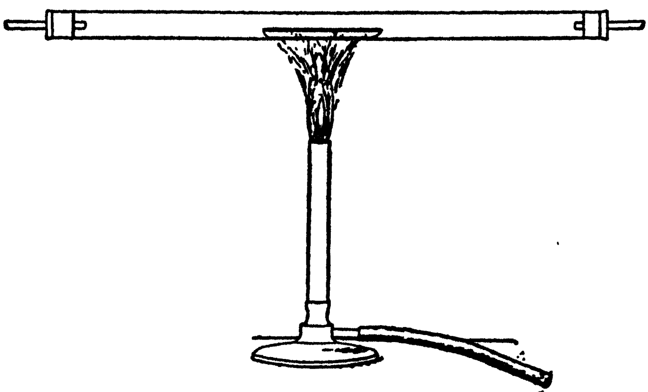


FIG. 17. Heating Copper in Oxygen.

The formation of cupric oxide takes place rapidly. If we limit the oxygen, part of the copper may remain unaltered; if we use it freely, the excess will pass on unchanged. A given weight of copper cannot be induced to take up more than a certain amount of oxygen, and use of a less amount simply limits the amount of copper transformed into oxide. The original weight of the copper, and the increase in final weight, representing oxygen, give us the data for determining the **composition** of cupric oxide. The data furnished by one rough lecture-experiment, for example, were as follows:

Weight of boat + copper	4.278 g.
Weight of boat empty	3.428 g.
Difference = weight of copper	0.850 g.

Weight after addition of oxygen	4.488 g.
Weight without oxygen	4.278 g.
Difference = weight of oxygen	0.210 g.

The proportion of copper to oxygen, so far as this one measurement goes, is therefore 85 : 21.

The results of quantitative experiments like the above are usually recorded in the form of parts in one hundred. To find the percentage of each constituent, we observe that the proportion of copper is 85 : 85 + 21, or $^{85}/_{106}$ of the whole. That of the oxygen is $^{21}/_{106}$ of the whole. Thus the percentages are:

Copper,	$106 : 85 :: 100 : x$	$x = 80.2$
Oxygen,	$106 : 21 :: 100 : x'$	$x' = 19.8.$

Naturally, the mean of the results of a number of more carefully managed experiments will be nearer the true proportions. The percentages at present accepted as most accurate are 79.9 and 20.1.

In the case of mercuric oxide, we may decompose a known weight of the oxide (p. 23) and afterwards weigh the mercury and ascertain the oxygen by difference.

The following figures show the results of some experiments like these, and represent the percentage compositions of the products. The numbers in brackets will be explained presently:

(1) **Cupric oxide**			(2) **Mercuric oxide**		
Copper	79.9	$\left[\frac{63.6}{16}\right]$	Mercury	92.61	$\left[\frac{200.6}{16}\right]$
Oxygen	20.1		Oxygen	7.39	
(3) **Water**			(4) **Chlorine monoxide**		
Hydrogen	11.19	$\left[\frac{2.016}{16}\right]$	Chlorine	81.8	$\left[\frac{70.92}{16}\right]$
Oxygen	88.81		Oxygen	18.2	

Combining Proportions. — The percentages in the above list represent the true proportions by weight in the various compounds, but naturally the individual numbers constituting those proportions have no chemical significance whatever. They are arbitrary values selected so that the two factors in the proportion may together make 100. Each pair represents the constant ratio which is the mean result of numerous careful experiments.

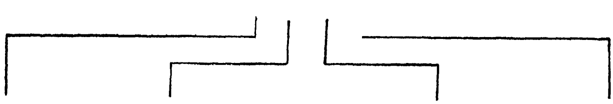
We begin the effort to reduce these numbers to order by selecting one element as our starting-point, and by taking some convenient weight of it as the basis. As we shall see, it makes *no difference*

what choice we make in either respect. To avoid waste of time, we shall, therefore, use oxygen, as it is the element generally preferred by chemists for the purpose. The reason for this preference will be apparent later (see pp. 50–2).

We should naturally be inclined to use 1 part of the element as our basis. But our later steps involve finding out what amounts of the other elements combine with this quantity, and we perceive (p. 48) that the amount of hydrogen in the case of hydrogen peroxide will be only 0.063 part. If, however, we take 16 parts of oxygen, this amount of hydrogen is also increased sixteen times and becomes 1.008. As no element is found to combine in smaller proportions than hydrogen, we are satisfied that a scale for our numbers based on 16 parts of oxygen will not involve any values less than 1. The choice of scale, as will be emphasized repeatedly, is purely one of convenience.

We now proceed to calculate from the above data the weight of each of the other four elements which combines with 16 parts of oxygen in the particular compounds listed. From (1) we calculate this weight of copper, thus 20.1 : 79.9 :: 16 : x (= 63.6 parts of copper). Similarly we find that 16 parts of oxygen combine, in (2) with 200.6 parts of mercury, in (3) with 2.016 parts of hydrogen, and in (4) with 70.92 parts of chlorine. Oxygen unites with almost all the known elements, and these four compounds have been chosen simply as a sample group.

Oxygen, 16



Copper, 63.6 Mercury, 200.6 Hydrogen, 2.016 Chlorine, 70.92

Now chlorine combines, not only with oxygen, but also with copper, mercury, and hydrogen, and measurement shows that *the combining proportions are represented, exactly, by the very same numbers listed above.* From the two independent facts that 16 parts of oxygen combine with 63.6 parts of copper and with 70.92 parts of chlorine, we could not possibly have foretold the proportions in which copper and chlorine would combine with one another. Yet measurement shows them to be 63.6 : 70.92 precisely. In the fol-

lowing table the proportions in which the elements combine with chlorine are placed under the corresponding parts of the names of the compounds with chlorine:

CUPRIC CHLORIDE	MERCURIC CHLORIDE	HYDROGEN CHLORIDE
63.6 : 70.92	200.6 : 70.92	2.016 : 70.92

If additional elements had been included in the group, a combining ratio could have been found for each, and seeming coincidences of the same nature would have multiplied rapidly. Thus, sulphur unites with hydrogen to give hydrogen sulphide. If, to maintain the same scale, we use 2.016 parts of hydrogen in expressing the proportion, we find that the combining ratio is 2.016 : 32.06. This result could not enable us to predict the proportion of copper to sulphur in cupric sulphide, but measurement shows it to be 63.6 : 32.06. Again, mercury and sulphur unite in the proportion 200.6 : 32.06. SULPHUR, with the value 32.06, may therefore be added to the series of combining proportions.

Law of Multiple Proportions. — One other remarkable fact remains to be noted. There are *two different* compounds of copper with oxygen. Cuprous oxide, the one not mentioned hitherto, is found in nature as a dark-red mineral which is entirely different from cupric oxide (p. 44) in physical properties. It can also be prepared in the laboratory, but not by simply passing oxygen over heated copper. Now, analysis shows that in cuprous oxide the proportion of copper combined with 16 parts of oxygen is 127.2. This new number for copper is not unrelated to the corresponding value in cupric oxide (63.6), for it is *exactly twice as great.* Again mercury forms mercurous oxide (see p. 48) as well as mercuric oxide, and in mercurous oxide the proportion of oxygen to mercury is 16 : 401.2. The proportions of mercury uniting with 16 parts of oxygen are therefore 200.6 and 2 × 200.6, and no other proportions are known. Still again, 2.016 parts of hydrogen unite with 16 parts of oxygen in water and 1.008 parts of hydrogen (*one-half* the former quantity) unite with 16 parts of oxygen in hydrogen peroxide. The fact suggested by these three examples is a general one. It was discovered by Dalton (1804) and was embodied by him in a statement known as the **law of multiple proportions,** which may be worded as follows: **If two elements unite in more proportions than one, forming two or more compounds, the quantities of one of the elements, which in the different compounds are united with identical amounts of the other, stand to one another in the ratio of integral numbers, which are usually small.**

The Law of Combining Proportions. — The reader should now examine carefully the following table of combining proportions. It includes *all* the compounds made up of pairs of the six sample elements under consideration, so far as the existence and composition of such compounds have been determined with certainty.

Cupric oxide 63.6 : 16	Mercuric oxide 200.6 : 16	Hydrogen monoxide (water) 2 × 1.008 : 16
Cuprous oxide 2 × 63.6 : 16	Mercurous oxide 2 × 200.6 : 16	Hydrogen peroxide 2 × 1.008 : 2 × 16
Cupric sulphide 63.6 : 32.06	Mercuric sulphide 200.6 : 32.06	Hydrogen sulphide * 2 × 1.008 : 32.06
Cuprous sulphide 2 × 63.6 : 32.06	Mercurous sulphide 2 × 200.6 : 32.06	Hydrogen chloride 1.008 : 35.46
Cupric chloride 63.6 : 2 × 35.46	Mercuric chloride 200.6 : 2 × 35.46	Sulphur monoxide 32.06 : 16
Cuprous chloride 63.6 : 35.46	Mercurous chloride 200.6 : 35.46	Sulphur sesquioxide 2 × 32.06 : 3 × 16
Chlorine monoxide 2 × 35.46 : 16	Sulphur monochloride 2 × 32.06 : 2 × 35.46	Sulphur dioxide 32.06 : 2 × 16
Chlorine dioxide 35.46 : 2 × 16	Sulphur dichloride 32.06 : 2 × 35.46	Sulphur trioxide 32.06 : 3 × 16
Perchloric anhydride 2 × 35.46 : 7 × 16	Sulphur tetrachloride 32.06 : 4 × 35.46	Sulphur tetroxide 32.06 : 4 × 16

It will be observed that the same number serves always to express the combining proportions of a given element, provided that multiplication by an integer is permitted when necessary. There are also many combinations of *three* of the same elements in one compound. But even in such cases the fundamental numbers still reappear. Thus oxygen, chlorine, and hydrogen combine in the proportions:

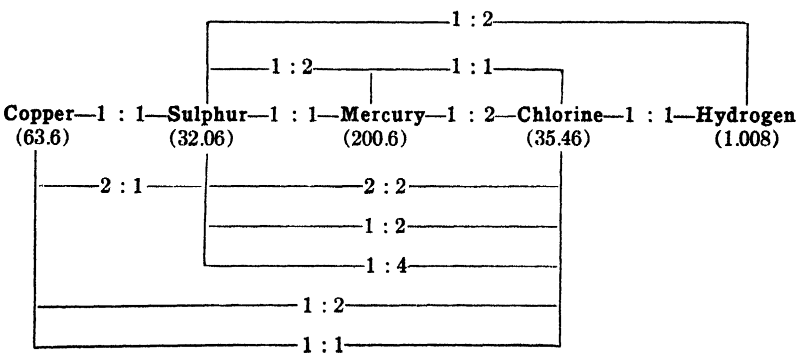
$$16 : 35.46 : 1.008, \quad 3 \times 16 : 35.46 : 1.008, \quad \text{and } 4 \times 16 : 35.46 : 1.008.$$

Nor is the recurrence of a fundamental number an exclusive property of the six elements we have chosen for illustration. A vast table containing every known element, and every compound of

* It may be noted here that several unstable compounds of hydrogen and sulphur are known, in which the combining proportions by weight of the two elements are represented by different integral multiples of the fundamental values 1.008 and 32.06. These compounds are not included in the above table for space considerations. Two unstable compounds of chlorine and oxygen (see p. 382) are also omitted.

every element, if prepared in the same way as that given above (by starting with a fixed number for one element and calculating the combining proportions in all the compounds with this number as a basis), would show that every element uses an individual, fundamental number, or integral multiples of this number, in every one of its combinations. No exceptions to this rule would be found in the whole mass of data except in a case such as lead from a radioactive source (p. 43).

These relations become clearer when represented diagrammatically. Thus the five elements, omitting oxygen, give the following compounds and no others:



It will be observed that hydrogen forms stable compounds with only two of the other four elements in the series. If, however, oxygen had been included, compounds of oxygen with all the other five would have demanded recognition. This illustrates the reason (see pp. 50–2) for the preference of oxygen as the fundamental element.

The law of combining proportions may be put briefly thus: **In every compound substance, the proportion by weight of each element may be expressed by a fixed number, one for each element, or by a multiple of the number by some integer (whole number).** It describes what is perhaps the most striking of all the characteristics of chemical action. Clearly it does not apply to mixtures, for any irregular proportion could be used in the physical process of mixing.

It is, perhaps, hardly necessary to point out that the law of multiple proportions is simply a partial statement whose whole content is included in this far greater generalization. No one chemist succeeded in discovering this prop-

erty of combining proportions. The work of J. B. Richter, Dalton, and many others contributed to it.

Most of the first exact determinations of combining proportions were made by Berzelius before 1830. It should be added that, while the individual fundamental numbers for the various elements, with the exception of that of oxygen which is the standard, are never actually whole numbers (although they remarkably often approach such integral values), the integers used to multiply them, when they are employed to express combining parts by weight, are so most exactly. Even in determinations by methods of the highest refinement, the factors to be used in multiplying the combining proportions are never found to diverge from whole numbers by amounts exceeding the known errors of the method of measurement.

The law of combining proportions has a corollary — misnamed the **law of reciprocal proportions** — which we shall merely state here: *If three elements, A, B, and C combine together in pairs, then the quantities of A and of B that combine with a fixed quantity of C bear a simple relation to the quantities of A and of B that combine with one another.*

Reëxamination of Combining Proportions. — If the reader will now reëxamine carefully the way in which the data were handled, the following significant questions will arise:

1. Oxygen was made the starting-point of the system and the value 16 was assigned to it as a fundamental combining number. If a different value had been used, would the combining numbers derived for other elements have been different? Yes, but the change would have affected all the numbers in the same ratio and so only the *scale* of the numbers would have been changed. An individual combining number, one for each element, would have still recurred wherever the element itself appeared.

2. The question might very well be asked: "Why select oxygen = 16 as a standard? Why not rather use hydrogen = 1?" Hydrogen is the element with the lowest combining proportions, and it would seem more natural to select this as our unit rather than to give it the awkward value of 1.008. In fact, hydrogen = 1 *was* employed as a standard by chemists for many years, and it led to a great deal of confusion. Hydrogen combines directly with very few other elements, whereas oxygen combines directly with almost all. We can obtain the exact combining proportions of most elements with respect to oxygen very easily, but the accurate determination of the hydrogen-oxygen ratio in water (see p. 158) is a matter of much greater difficulty. As soon as chemists awoke to the fact that

it was necessary for them, under the hydrogen standard, to change the atomic weight of almost every element on the list every time some ingenious person redetermined the hydrogen-oxygen ratio a little more accurately, they very sensibly decided to go over to the more rigid oxygen basis. Even although we have succeeded more recently in fixing the hydrogen-oxygen ratio very exactly, new reasons have also developed, as will appear later (p. 478), which support our decision not to shift back.

3. Even the use of another element as the initial one would not have prevented the discovery of the law. Thus with copper as the initial element, and the value 63.6, no change whatever would have been noted. With a different value for copper (such as 1 or 127.2), a change of scale in all the numbers would have followed, but individual combining values would have appeared just as certainly as before.

4. The basic number for expressing the combining proportions of chlorine in all the compounds listed in the table on p. 48 is given as 35.46, whereas the first compounds of this element examined in an earlier section (p. 47) suggested the value 70.92, or 2×35.46. The thoughtful student will undoubtedly be puzzled as to the explanation of this change, and may quite fairly put the question: "What reason have we for expressing the combining proportions of the elements in hydrogen chloride as 1.008 : 35.46 rather than as 2.016 : 70.92?" The preferred method of presentation becomes still more provoking when the combining proportions given for the constituent elements of hydrogen peroxide ($2 \times 1.008 : 2 \times 16$) are noted. Again the question will arise: "Why is not the simpler ratio 1.008 : 16 used instead?"

The answer to these and other questions will be developed in subsequent chapters (IV and XI). For the present, the beginner must be satisfied by the statement that the values selected, apparently in a perfectly arbitrary way, are those which are actually employed by chemists in all their work. It is clearly advisable, therefore, that he should become accustomed to using them at once. Alternative values which would suit the immediate argument just as satisfactorily would be merely a source of confusion later, and the various reasons which justify the preference for the numbers here chosen will be fully discussed as soon as opportunity arises.

The importance of the fact described in the law of combining proportions cannot be emphasized too strongly. Without this fact, the remembering of the compositions of chemical substances, necessary as it is to the chemist, would have been completely beyond the power of any ordinary memory

With it, the task becomes comparatively simple. It is only necessary to decide on the best system of values for the combining proportions, and then, *regarding the value of this for each element as the unit of weight for that element,* to express the proportions of the element in every compound by the proper multiples. Thus, given a list of the combining numbers, one for each element, only the small integral multiples have to be kept in mind in connection with each compound.

The reader will require a little time, however, before he becomes accustomed to the use, not of a single unit of weight, but of a different one for each element. Chemistry is the only science in which the physical unit of weight, which is the same for all materials, is not employed for every purpose. The physical manipulations of the chemist are carried out with the use of physical units, but the chemical results are expressed in terms of individual unit quantities of the several elements, the combining proportions by weight.

In the historical development of the science, it must be mentioned, the usual basis for expressing the combining proportions of the elements in their compounds has been either oxygen = 8 or hydrogen = 1. Some of the advantages of an oxygen over a hydrogen scale have already been discussed. The reasons for the employment of the scale oxygen = 16 in preference to the scale oxygen = 8 will appear in the course of subsequent chapters.

The term "combining weights" has also been considerably used in the past as an abbreviation for "combining proportions by weight." The employment of this contraction has been discarded here, because of the opportunities which it offers for confusion later with the terms "atomic weights" and "equivalent weights." These two latter terms, as we shall see, are essentially referred each to a single basis, and neither has any meaning in chemistry apart from its fixed basis. The law of combining proportions, on the other hand, is fundamentally independent of the basis selected, as has been emphasized repeatedly in the preceding sections. It is true that we have, for reasons of convenience, utilized the scale oxygen = 16 in illustrating and discussing the law, but the law would be just as valid, and just as important, on any other scale, with any other element as a standard. It deals with the "proportions by weight" in which elements combine, not with the weights themselves. As soon as we go beyond the mere consideration of proportions and deliberately limit ourselves to a single scale, we have left the field of combining proportions and entered the domain of atomic and equivalent weights. The use of the term "combining weights" tends to leave the student stranded half-way between the two fundamentally distinct ideas, and its continuance is therefore not to be recommended.

Exercises. — 1. For the purpose of recording the results of quantitative experiments, why do we prefer percentages (p. 45) to the actual weights themselves?

2. To test the correctness of the statements on p. 51, par. 3, take mercury as the basal element and 250 as its combining proportion by weight, and work out from the data on p. 48 the corresponding combining proportions of the other five elements. Then show that the values obtained have the same fundamental property as have those listed in the table on p. 49.

3. Show how the five oxides of nitrogen in the following table illustrate the law of multiple proportions:

Compound	*Percentage Composition*	
Nitrous oxide	Nitrogen 63.63	Oxygen 36.37
Nitric oxide	" 46.67	" 53.33
Nitrous anhydride	" 36.84	" 63.16
Nitrogen tetroxide	" 30.44	" 69.56
Nitric anhydride	" 25.93	" 74.07

4. Show how the following oxides of iron illustrate the law of multiple proportions:

Iron (223.36) + Oxygen (96) → Ferric oxide (319.36)
Iron (167.52) + Oxygen (64) → Magnetic oxide of iron (231.52).

5. Calculate the percentage compositions of (*a*) ordinary lead chloride, (*b*) lead chloride prepared from uranium-lead with a combining proportion of 206.1 on the basis oxygen = 16, (*c*) lead chloride prepared from thorium-lead with a combining proportion of 208.4 on the same basis (see p. 43).

6. Show how the following reactions illustrate the law of reciprocal proportions: (*a*) Zinc (65.37) + Sulphur (32.06) → Zinc sulphide (97.43); (*b*) Zinc (130.74) + Oxygen (32) → Zinc oxide (162.74); (*c*) Sulphur (32.06) + Oxygen (32) → Sulphur dioxide (64.06).

7. Show how the following reactions illustrate the law of reciprocal proportions: (*a*) Iron (222.36) + Oxygen (96) → Ferric oxide (319.36); (*b*) Iron (55.84) + Sulphur (32.06) → Ferrous sulphide (87.90); (*c*) Sulphur (32.06) + Oxygen (32) → Sulphur dioxide (64.06).

READING REFERENCE

Kendall; At Home among the Atoms, Chapter V.

CHAPTER IV

THE ATOMIC THEORY. ATOMIC WEIGHTS AND CRYSTAL STRUCTURE

Explanation of the Law of Combining Proportions: Atoms and Molecules. — To *explain* the law of combining proportions by weight it was found necessary to use the third kind of explanation (p. 34), namely, the making of a hypothesis. The details of *how* two substances combine cannot actually be seen, so chemists had first to *imagine,* and then to justify by experiment, some postulates which would account for the possession of an individual fundamental number by each element in all its compounds. If oxygen, for example, *is composed of minute, invisible particles,* which are *all alike in weight,* and hydrogen, sulphur, and the other elements are of the same nature, except that *the weight of the particle of each kind of element is different,* we have the basis of an explanation. We have to suppose, further, that, when elements combine, *the individual particles adhere in pairs or groups, or arrange themselves in a regular pattern,* **as wholes,** *and are never broken.* In this way the particle of each variety of elementary matter will have a definite, unchangeable weight, which will be one of its fixed properties, whether free or in combination.

If, now, the relative weights of the *particles* of oxygen, copper, and hydrogen are in the proportions of the numbers in the table on p. 48, namely, 16 : 63.6 : 1.008, the whole situation becomes clear. Chemical union must consist, in detail, in the coördination of the particles of the elements to form the particles of the compound. For each particle of cupric oxide (p. 45) the proportion 63.6 : 16, or one particle of copper (63.6) to one particle of oxygen (16), is required. For each particle of water, where the proportion of oxygen to hydrogen is 16 : 2.016 (or 2 × 1.008), evidently one particle of oxygen and *two* particles of hydrogen are necessary. Varying, intermediate proportions are impossible, because the particles of the elements are permanent, are never broken, and combine as wholes in a uniform way through the mass. The only possible variation would be to take different relative numbers of the particles — for example, two of oxygen to two of hydrogen (2 × 16 : 2 × 1.008). But this product would have a different composition

from water, and would not be water. This compound, with the double proportion of oxygen, is indeed known (it is hydrogen peroxide), and is the only other known compound of these two elements.

Atoms and Molecules. — This explanation of the law of combining proportions was first offered by Dalton, a schoolmaster of Manchester, in 1802. Borrowing an idea from the speculations of the Greek philosophers, he called the particles of elements **atoms** (Greek, ἄτομος, not cut, or not divided). The pairs or groups which result when individual atoms of different elements come together, or the units of the pattern in which they arrange themselves, Dalton called **molecules** (diminutive of Latin *moles,* a mass).

The chemical combination of two simple substances A and B apparently consists, then, in an elaborate re-grouping of the atoms of both elements into a fixed design, and if we could isolate and examine single "molecules" of the compounds, we should find that they were all uniform in containing atoms of A and B in the same simple whole-number ratio.

This explanation is called the **atomic theory.** For long it remained a mere hypothesis. Recently, however, we have obtained several independent proofs that molecules and atoms are real, for we can now count and weigh the individual particles, and we even know something of the actual structure of the atoms. The fundamental numbers derived in the last chapter, one for each element, are now seen to represent **the relative weights of the atoms on the basis Oxygen = 16,** and will therefore be called henceforth **atomic weights.**

Atomic Weights. — The following list shows the accepted atomic weights for all the elements whose combining proportions by weight we have discussed so far, along with one or two others, added by way of furnishing a fair sample:

Element	Atomic Weight	Element	Atomic Weight
Oxygen	16	Iron	55.84
Copper	63.57	Magnesium	24.32
Sulphur	32.06	Carbon	12.00
Mercury	200.61	Aluminium	26.97
Chlorine	35.46	Sodium	23.00
Hydrogen	1.008	Bromine	79.92

These values, it must be noted, all refer to the fixed basis oxygen = 16, and have no significance apart from that basis. A complete list of the atomic weights for all the elements (save a few, not yet exactly determined) is given inside the rear cover of this book. These numbers will hereafter be in constant use.

Frequently, as in the list on p. 55, we shall employ approximate values which do not carry the atomic weights for certain elements to the last place of decimals given in the table on the rear cover. This latter table presents the figures recommended by the International Committee on Atomic Weights in its 1936 Report as the most probable values, based on the results of the most accurate analytical determinations. It is always possible that later experimentation will demonstrate some unsuspected error, even in a long-accepted value, so that for illustrative purposes the rounding-off of the last figure is quite legitimate.

To the reasons already given for the choice of oxygen as the fundamental element, and the value 16 for its atomic weight, one other may now be added. The majority of the atomic weights, calculated on this basis from the experimental results, fall so close to being integers that the nearest round numbers are exact enough for ordinary use. Thus in the above list seven of the twelve atomic weights are within 0.1 of the nearest whole number. This convenience disappears when, for example, hydrogen with the value 1 (instead of 1.008) is made the basis. The explanation for this will appear later (see pp. 478–82).

In one important detail the original theory of Dalton has recently been found to be inaccurate, namely in postulating that atoms of the same element are all alike in weight. Many elements, in point of fact, have been shown to contain *two or more distinct kinds of atoms, identical in their general chemical properties, but differing essentially in mass.* Such varieties of the same element are called *isotopes* (see p. 43). Thus *chlorine* consists of an intimate mixture of two isotopes of mass 35 and of mass 37, in such proportions that the *average* atomic weight is 35.46. This point will be discussed more fully in a subsequent chapter (see p. 476). At the present stage it will suffice to mention that, inasmuch as all naturally-occurring chlorine has exactly the same average atomic weight, and no method for the large-scale separation of the two isotopes has yet been devised, we may continue to use, in our ordinary chemical work, 35.46 as the atomic weight of chlorine and may still regard our fundamental chemical laws, such as the law of definite proportions, as valid in all of their practical applications.

A Warning. — From what has been said in the last chapter (p. 51), it will be evident to the student that the values selected for

the various atomic weights have not thus far been fully justified.

The number of known compounds is so enormous, and there are so many instances of the law of multiple proportions in chemistry, that the first value which we may derive for the combining ratio of any given element (*e.g., copper*), by the analysis of only a few of its compounds selected at random, will obviously not necessarily be the value which we shall find it most convenient to employ in a final tabulation, after we have studied the various types of compounds which contain the element in a more exhaustive manner. Thus, if we had happened to approach copper by way of cuprous oxide (p. 47), we should have deduced the combining proportion 127.2 for the element, and cuprous chloride would, apparently, confirm this value. In the case of other elements, such as chlorine, as will be evident from a study of the table on p. 48, a still more varied selection of values might easily be arrived at, according to the particular compounds favored. It is most important to note, however, that *in all such cases the law of multiple proportions invariably applies exactly*, and that although the first value chosen for the combining ratio of an element may later be modified, such modification must be limited (see the next section) to a multiplication or a division of this value by a simple small integer, and can never result (unless the scale is changed) in a number entirely unrelated to the original selection.

No facts discussed in the preceding paragraphs, then, can enable us to come to any final decision even upon the *relative* weights of the atoms, much less to establish their *absolute* values. Some of the lines of attack, however, by means of whch this difficult task has ultimately been accomplished will be developed in the following sections. In a later chapter (Chap. XI), additional facts will be encountered which enable us to confirm the conclusions therein drawn.

Dulong and Petit's Law, a Simple Means of Determining Atomic Weights. — It was first suggested (1818) by Dulong and Petit, of the École Polytechnique in Paris, that when the **atomic weights of the elements are multiplied by the specific heats of the simple substances in the solid condition, the products should be approximately the same in all cases.** In other words, the specific heats of the elements are inversely proportional to their atomic weights. The following table, in which round numbers have been

used for the atomic weights, shows that the product of the two factors lies usually between 6 and 7, averaging about 6.4:

Element	Atomic Wt.	Sp. Ht.	Product	Element	Atomic Wt.	Sp. Ht.	Product
Lithium.....	6.9	0.94	6.6	Iron...........	55.8	0.112	6.3
Sodium......	23.0	0.29	6.7	Copper.......	63.6	0.095	6.0
Magnesium..	24.3	0.245	6.0	Zinc...........	65.4	0.093	6.1
Silicon......	28.1	0.16	4.5	Bromine (solid).	79.9	0.084	6.7
Phosphorus (white)....	31.0	0.20	6.2	Gold..........	197.2	0.032	6.3
				Mercury (solid).	200.6	0.0335	6.7

In the case of several metals the atomic weights in common use in 1818 needed to be reduced to one-half or one-quarter to bring them into accordance with this simple rule, but the new values proposed by Dulong and Petit were ultimately agreed to by their colleagues, and the law has very frequently been called into service since to decide between the several possible values for particular elements. Copper (see the preceding section) may be taken as an example — is its atomic weight 63.6 or 127.2? Berzelius preferred the higher figure, but the specific heat of the metal is 0.095, which indubitably leads to the lower value ($63.6 \times 0.095 = 6.0$). Although the product 6.4 is only approximate, so that the *exact* atomic weight of an element cannot be deduced from its specific heat alone, yet the law of Dulong and Petit suffices us to select with confidence the true value from the various multiples and sub-multiples that may also be suggested by the combining proportions in different compounds. *We choose that figure which, when multiplied by the specific heat, gives approximately 6.4,* and the difficulty discussed on page 57 is thus solved.

Another way of expressing the law of Dulong and Petit will give it greater chemical significance. The specific heats are the amounts of heat required to raise one gram, that is, one *physical* unit, of each element through one degree. When we multiply this by the atomic weight, we obtain the amount of heat required to raise one gram-atomic weight of the element, that is, one *chemical* unit, through one degree. The values of this product (the "atomic heat") are approximately equal. Since there are equal numbers of atoms in one gram-atomic weight of each element, it follows that: **Equal amounts of heat raise equal numbers of atoms of all elements in the solid state through equal intervals of temperature.**

The law of Dulong and Petit, formerly regarded as purely em-

pirical, is now theoretically established, and is especially useful **for fixing the atomic weight of an element of which no volatile compounds are known** (see p. 195).

The conspicuous exceptions to the law occur among the elements with low atomic weights only. The products for four of these, the atomic weights being given in parentheses, are as follows: Beryllium (9), 3.7; boron (11), 2.8; carbon (12), 1.7; and silicon (28.1), 4.5. Further investigation shows, however, that in the case of precisely these elements the value found for the specific heat under constant volume, which is the property strictly concerned, increases very rapidly, at low temperatures, with the temperature at which the specific heat is measured, but approaches a constant normal value at high temperatures. Thus at 985° the specific heat of the diamond (carbon) is 0.45, which when multiplied by the atomic weight gives the product 5.5. So that even the exceptional elements tend to come into line when the specific heat is measured at higher temperatures — and Dulong and Petit's statement has been shown by later investigators to be necessarily limited to such temperatures.

The Properties of Solids. — The fact, noted in the preceding section, that equal amounts of heat raise equal numbers of atoms of all elements in the solid state through equal intervals of temperature leads us to consider at this point the general structure of matter in the solid state.

True solids are sharply distinguished from liquids by their *crystalline forms.*

A crystal arises by growth. When the process is watched, as it occurs in a freezing liquid or an evaporating solution, the slow and systematic addition of the material in lines and layers, as if according to a regular design, is one of the most beautiful and interesting of natural phenomena. The fern-like patterns produced by ice on a window-pane show the general appearance characteristic of crystallization in a thin layer. A larger mass in a deep vessel gives forms which are geometrically more perfect. From its very incipiency the crystal has the same form as when, later, its outlines can be distinguished by the eye. Hence the outward form is only an expression of a specific internal structure which the continual reproduction of the same outward form on a larger and larger scale leaves as a memorial of itself in the interior.

Crystalline form is so continually used in identifying (p. 29) the substances produced in chemical actions that a list of the kinds of forms which occur will assist in giving definite meaning to our descriptions.

The classification of crystalline forms is carried out according to the degree of symmetry of the crystals. Thirty-two distinct classes

are recognized, but for our purpose a rougher division into six groups will suffice. These groups are known by the following names:

1. Regular system.
2. Tetragonal prismatic system.
3. Hexagonal system.
4. Rhombic system.
5. Monosymmetric, or monoclinic, system.
6. Asymmetric, or triclinic, system.

The **regular system** presents the most symmetrical figures of all. Some forms which commonly occur are the octahedron (Fig. 18) shown by alum, the cube (Fig. 12, p. 31) affected by common salt, and the dodecahedron (Fig. 19) frequently assumed by the garnet.

The **tetragonal prismatic system** includes less symmetrical forms than the previous one, since the crystals are lengthened in one direction. Fig. 20 shows the condition in which zircon (zirconium oxide), which furnishes us with the basis of certain electric lamp filaments, occurs in nature. The form of ordinary hydrated nickel sulphate is similar to this.

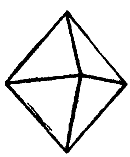


FIG. 18. Octahedron (Alum).

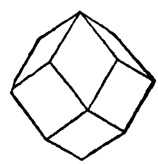


FIG. 19. Dodecahedron (Garnet).

The **hexagonal system,** like the preceding, frequently exhibits elongated prismatic forms, but the section of the crystals is a hexagon instead of a tetragon and the termination is a six-sided pyramid. Quartz (Fig. 1, p. 6), or rock crystal, is the most familiar mineral in this system. Calcite, which is chemically identical with

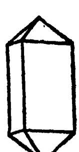


FIG. 20. Square Prismatic (Zircon).

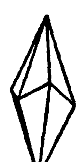


FIG. 21. Scalenohedron (Calcite).

chalk, or marble, takes forms known as the scalenohedron (Fig. 21) and rhombohedron (Fig. 22), which are classified in a subdivision of this system.

The **rhombic system** includes the natural forms of the topaz, and of sulphur (Fig. 7, p. 20), as well as those of potassium permanganate (Fig. 23), potassium nitrate (Fig. 24), and many other sub-

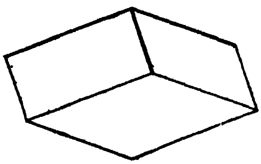


FIG. 22. Rhombohedron (Calcite).

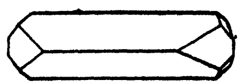


FIG. 23. Rhombic (Potassium Permanganate).

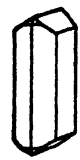


FIG. 24. Rhombic (Potassium Nitrate).

stances. These crystals exhibit a good deal of symmetry, but their section is always rhombic, and hence the name.

The **monosymmetric system** exhibits forms which have but one plane of symmetry. Gypsum (Fig. 25), which is hydrated calcium sulphate, and feldspar (Fig. 3, p. 6) are minerals possessing forms of this kind. Tartaric acid, rock candy (Fig. 26), potassium chlorate,

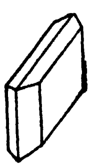


FIG. 25. Monosymmetric (Gypsum).

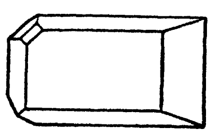


FIG. 26. Monosymmetric (Rock Candy).

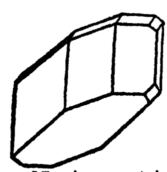


FIG. 27. Asymmetric (Blue-stone).

and hydrated sodium carbonate (washing soda) belong to this system.

The **asymmetric system** includes forms which have no plane of symmetry whatever. Blue-stone (Fig. 27), the ordinary hydrate of copper sulphate, is one of the most familiar substances of this kind.

The forms of crystals which we may actually make seldom correspond exactly with the figures. If we allow a crystal to grow upon the bottom of a vessel, for example, it will usually have a tendency to spread itself out parallel to the surface of the glass, and when taken up for examination, will be found to present a somewhat distorted form. By changing, at frequent intervals, the face on which the crystal stands, however, uniform growth in all directions is secured. Hanging a small crystal by a thread insures almost

ideal development. Yet the form even of distorted crystals can readily be recognized by suitable means. The shape of the faces may indeed be extremely misleading. We find, however, that the angles at which the faces meet are always the same, whatever disproportionate growth may have occurred in the development of the crystal.

Since, in general, each substance has a form of its own, no other substance, as a rule, can be used even partially in building up the crystal (see, however, Isomorphism). This fact is taken advantage of in order to separate chemical substances from impurities. The impure body is first dissolved in some solvent. The preponderating substance in the mixture, unless it is very much more soluble than the impurity, will then usually give pure crystals while the foreign body remains in solution.

The tenacity of crystals, to whatever system they may belong, is different in different directions. Thus, a crystal of salt has a cleavage parallel to any of the faces of the cube, and, therefore, splits most easily in one of three directions at right angles to each other. Calcite, whatever the outward form of the crystal, always cleaves so as to give a rhombohedron. Fluorite (p. 355), although almost always cubical in form, splits when broken so as to give an octahedron.

The shapes of gems must not be confused with crystalline forms. The original crystals are cut and polished to a new form specially adapted to increase the ornamental value of the stone by causing it to reflect more light (see Diamond). Again, glass is apparently solid, yet it has no structure or form of its own. The word "crystal" applied to cut glass would therefore be misleading if taken literally.

Substances such as glass,* which do not exhibit any specific crystalline form, although commonly called solids, are strictly speaking still in an extremely viscous liquid state (see p. 664). In true liquids and gases, the cohesive forces between adjacent particles are exercised equally in all directions, with the result that the particles are all in haphazard, unordered positions relative to one another and no particular arrangement in space persists. In glass, which is a *supercooled liquid* (see p. 207), sub-microscopic crystal nuclei do exist, but have not succeeded in coalescing into any definite continuous structure. Substances of this kind are therefore called **amorphous** (Greek, *without form*). In true crystals, on the other hand, since each substance shows an individual geometrical form, the forces between adjacent particles must be exercised *in definite directions.*

Crystal Structure. — Exterior crystal form, as we have seen (p. 7), is a specific property which is of great service in the *recog-*

* *Strictly speaking,* of course, glass is not a *single substance,* but it is the simplest familiar material which illustrates the point under discussion.

nition of a substance, and a whole distinct science — crystallography — is devoted to its study. In chemistry itself, however, interest in recent years has centered upon the *interior arrangement* of the particles which compose the crystal lattice.

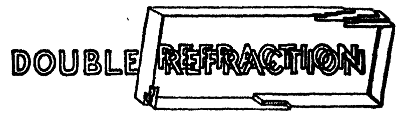


FIG. 28. Double Refraction (Calcite).

The fact that crystals possess definite planes of cleavage has long been taken to indicate that these particles are arranged in a regular pattern in each crystal. The study of the effect of certain crystals on ordinary light has brought up some interesting points, such as double refraction (exhibited by calcite, Fig. 28). No final information regarding the arrangement of the particles in the interior of a crystal was obtained, however, until X-rays were utilized instead of visible light.

X-Rays. — The production of X-rays takes place as follows: In an evacuated tube, through which an electric discharge is passed (Fig. 29), the "rays" emanating from the cathode (**cathode rays**) strike the anti-cathode and the glass beyond it. Cathode rays were discovered by Sir William Crookes (1878), and later were shown

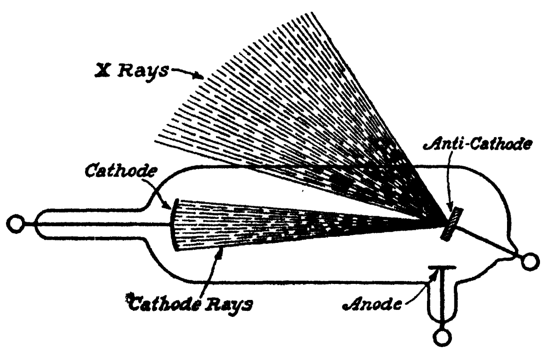


FIG. 29. X-Ray Tube.

to consist of particles of negative electricity or **electrons,** each having a mass about $\frac{1}{1850}$ of that of an atom of hydrogen (see p. 472). They reproduce in the glass a greenish-yellow, fluorescent light. Röntgen (1895) accidentally discovered that this light (**X-rays**) penetrated paper, flesh, and other materials composed of elements of low atomic weight and acted upon photographic plates.

Visible light, X-rays, and wireless electric waves are all vibrations of the same nature. They differ only in wave-length, the order of the wave-lengths being 10^{-5} cm.,* 10^{-8} cm., and 10^{5} cm. (1000 meters), respectively. Now, just as the spectrum of visible light is obtained by using a ruled grating, on which the lines are separated by distances of the order of the wave-lengths of such light, so ordinary crystals give spectra of X-rays, indicating that they are composed of particles arranged in rows about 10^{-8} cm. apart, which therefore form a suitable grating for X-rays. This fact was first discovered by Professor Laue of the University of Zürich (1912).

Laue's Method of Crystal Analysis. — Laue's method for determining the spatial arrangement of the rows of particles in any given crystal consists in directing a small pencil of X-rays through a thin film of the crystal in a direction parallel to an axis of symmetry and then allowing the rays to impinge on a photographic plate, when a diffraction pattern due to the crystal lattice is obtained (Fig. 30). Drawings from two typical Laue photographs, derived in this way with crystals of rock salt (sodium chloride) and rutile (titanium dioxide) respectively, are shown in Figs. 31 and 32. While the diagrams are exceedingly intricate (since the diffraction grating is three-dimensional) in most cases it is possible to calculate from the positions of the spots the ultimate crystal structure.

Bragg's Method. — For practical purposes, Laue's original method received a valuable supplement in 1913 in the **reflection method** of Bragg (Fig. 33), in which a beam (*AAAA*) of X-rays of definite wave-length λ is directed at an angle upon a face of the crystal. Successive planes of particles (p) reflect the rays, and it will be noted that the deeper a ray penetrates into the crystal before reflection occurs, the farther it must travel before it reaches an outside point C, where the reflected beam can be examined. The actual extra distance traveled, for each plane which is penetrated, is $2d$ sine θ, where d is the distance between the planes and θ the

*This is a method used in physics and chemistry to express numbers so large, or so small, as to be cumbrous and incomprehensible if written in the ordinary way. It means that the unit is to be followed by the number of zeros indicated by the exponent, when this is positive, or that it is to be preceded by the number of zeros (starting with that placed before the decimal point) indicated by the exponent, when this is negative. Thus $10^{-5} = 0.000,01$; $10^{-8} = 0.000,000,01$; $10^{5} = 100,000$; and so on.

angle of incidence of the beam on the face of the crystal. Now if θ is such that this distance, $2d$ sine θ, is equal to the wave-length λ of the beam employed, or is an integral multiple of this wave-length,

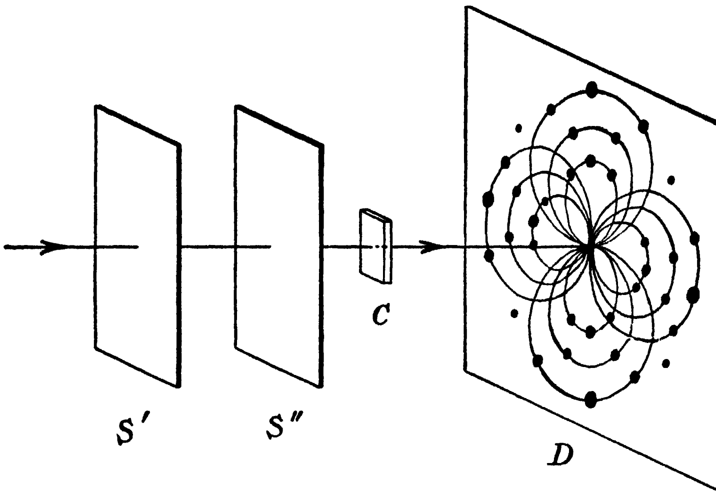


FIG. 30. Laue Method for the Determination of Crystal Structure.
The beam of X-rays, after passing through pin-holes in the lead sheets S' and S'', is broken up by the crystal C into a diffraction pattern, registered on the photographic plate at D.

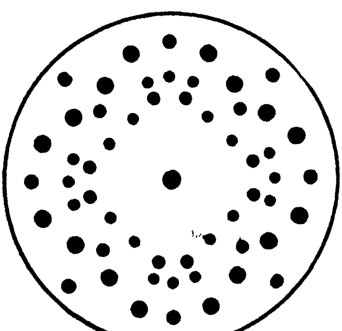


FIG. 31. A Laue Photograph of Rock Salt.

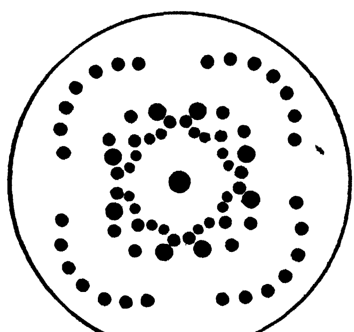


FIG. 32. A Laue Photograph of Titanium Dioxide.

then rays reflected from different planes will reinforce one another, crest to crest and hollow to hollow, whereas for all other values of θ the reflected waves will not fit exactly, and the different phases will consequently tend to neutralize each other. By noting the

reflection-angles, therefore, for various planes of the crystal, the elucidation of the arrangement of the particles in space is a comparatively simple matter.

If a large crystal of the substance to be analyzed is not available, then a third method — the **powder method** devised independently by Debye and Scherrer and by Hull — must be employed. In this method a narrow beam of X-rays of definite wave-length is passed through the finely powdered substance, pressed into a small cylinder. The minute crystals being in complete disorder in the compressed mass, a number of crystal faces will be in the positions of their reflection angles, and the reflected rays produce a pattern of fine lines upon a photographic film surrounding the cylinder. From the positions and intensities of these lines it is possible to calculate the lattice structure of the particles composing the crystal.

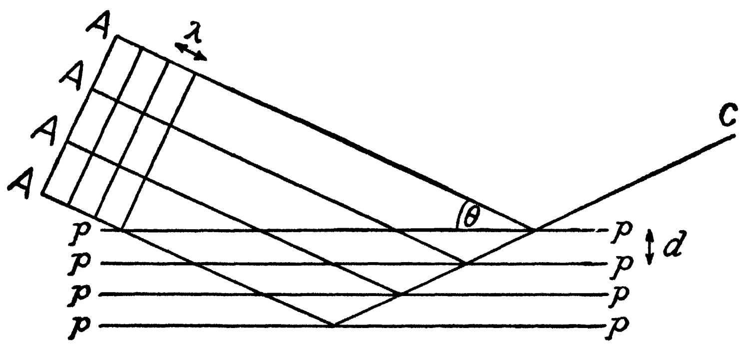
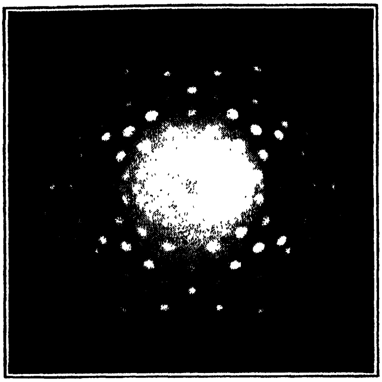
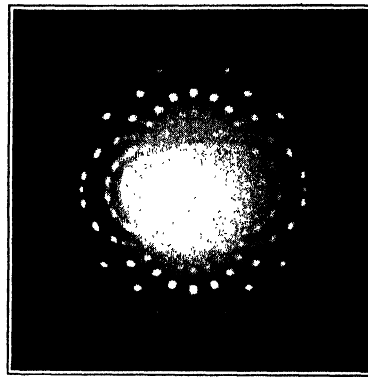


FIG. 33. Bragg Method for the Determination of Crystal Structure.

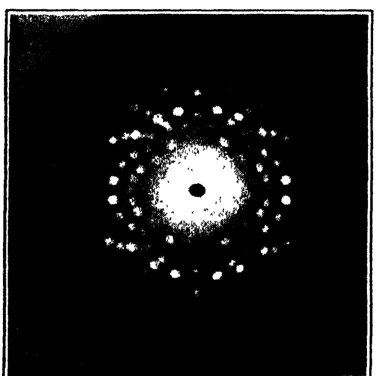
In interpreting the photographs obtained from crystals of elementary substances, it is obviously natural for us to assume that the exceedingly minute particles which build up the pattern of the lattice are the actual individual atoms, rather than aggregates of atoms, and statistical evidence in support of this assumption will be given later (p. 73). Even in the case of compounds, where we might be more disposed to expect the survival of compact aggregates of the component atoms so intimately conjoined in pairs or groups as to present to us a homogeneous molecular structure, all the experimental results indicate that the ultimate limit of division into distinct individual atoms is similarly attained (see p. 68). We shall, therefore, throughout the remainder of our discussion, employ the term "atoms" instead of "particles," and the justification of this procedure will become apparent as we proceed.



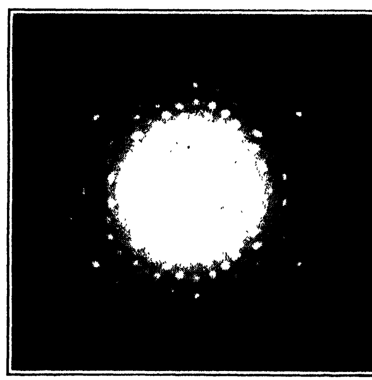
I



III



II

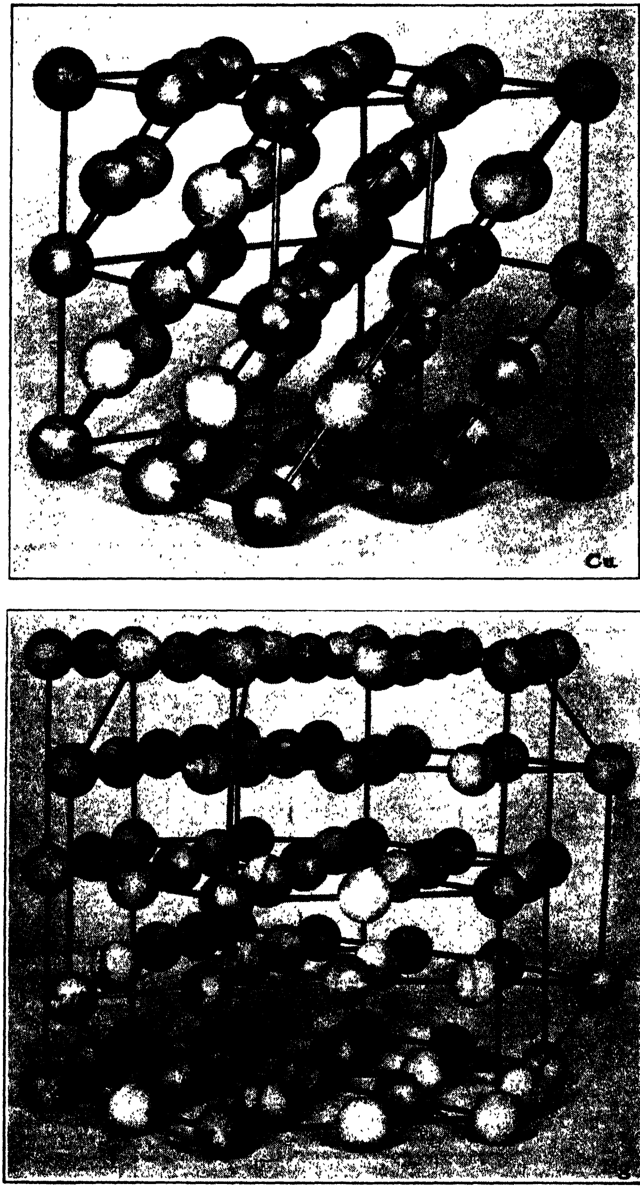


IV

TYPICAL LAUE PHOTOGRAPHS

I-III. ANHYDRITE IV. ARAGONITE

See page xix



ARRANGEMENT OF ATOMS IN COPPER AND MAGNESIUM

See page xx

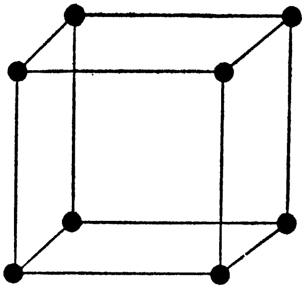


FIG. 34. Simple Cubic Lattice.

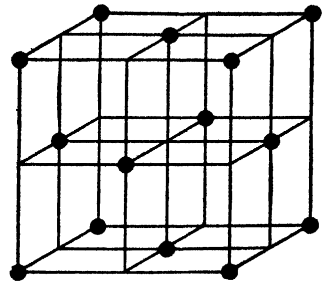


FIG. 35. Face-centered Cubic Lattice.

The Cubic Lattice. — A few of the simpler results may now be presented. A great many elements and compounds have been found to exhibit the most symmetrical of all arrangements, the **cubic lattice.** There are three ways in which atoms may be located in three dimensions to give a lattice of this elementary type, and these three ways are illustrated in Figs. 34, 35 and 36. In actual fact, it may be observed, the atoms do not exist at such wide intervals as represented in these diagrams, but are practically touching all of their nearest neighbors, so that in the simplest type of cubic lattice (Fig. 34) the side of the cube represents the sum of the radii of two adjacent atoms. The dots are reduced in the diagrams merely for the sake of clearness.

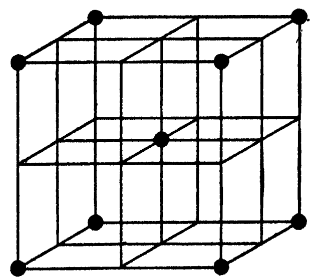


FIG. 36. Cube-centered Cubic Lattice.

The best example of the first type of cubic lattice — the simple cubic — is common rock-salt or sodium chloride. A detailed examination of the crystal structure of this compound is given in the following section. Potassium chloride, silver chloride, ammonium iodide, magnesium oxide, and calcium sulphide are all exactly similar to rock-salt in their structure. Most of the metals, however, exhibit a **face-centered** or a **cube-centered cubic lattice.** Fig. 35 represents the face-centered cubic lattice, which is given by aluminium, nickel, copper (see p. 73), silver, gold, and platinum, Fig. 36 represents, finally, the third type of cubic lattice — the cube-centered. This pattern is shown by sodium, potassium, chromium, iron (see p. 901), and tungsten.

Sodium Chloride. — This compound, as we have mentioned above, exhibits a simple cubic lattice structure, and it will be worth our while to study the arrangement of the atoms therein in detail. The pattern into which the atoms fall, as indicated by X-ray analysis, is shown in Fig. 37. This pattern is deduced as follows:

According to theory, the efficiency of a particle in scattering or reflecting X-rays should increase with increasing mass. If the unit particles in the sodium chloride lattice were *molecules of sodium chloride,* consequently, all of the particles should behave similarly as diffracting or reflecting centers. If, on the other hand, the *individual atoms* are the units, the difference between sodium (23) and chlorine (35.5) should be well marked on the photographic plates. A comparative analysis of the pictures obtained with different faces of the crystal shows that the latter assumption is correct. A cleavage plane along any of the sides of the cubes contains equal numbers of sodium atoms (Na) and of chlorine atoms (Cl), but a diagonal cleavage plane will contain either sodium atoms alone or chlorine atoms alone.

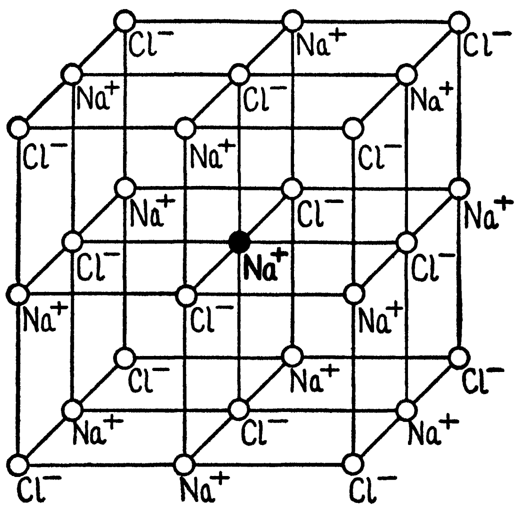


FIG. 37. Ultimate Structure of a Crystal of Common Salt.

If we concentrate our attention upon any particular atom in the rock-salt lattice (say the sodium atom distinguished by a black circle in the center of Fig. 37) we see that it is surrounded by six equidistant chlorine atoms. Similarly, each chlorine atom is sur-

rounded by six equidistant sodium atoms, and so the whole pattern goes on into space until the surface of the crystal is reached. Strictly speaking, then, we find that when sodium and chlorine combine to form sodium chloride, *there is no actual combination!* No sodium atom has coalesced with any specific chlorine atom to give a molecule of sodium chloride; each sodium atom is surrounded rather by six chlorine atoms, all of which are equally concerned with it and also with all similar adjacent sodium atoms. A compound like sodium chloride in the solid state, therefore, contains the atoms of its constituent elements arranged in a definite pattern, but without any specific partnership. The numerical ratio of the atoms of the two elements is, of course, fixed just as rigorously by the nature of the lattice as if particular partners were present, and the orderly atomic arrangement existent in the compound is something quite different from the crude intermingling which we obtain in a mixture. The side of each unit cube in the case of sodium chloride is only about one hundred millionth of an inch; in other words, there are approximately 10^{24} atoms in a single cubic inch of rock-salt.*

Electrons and Ions. — What keeps the atoms in a compound in place and prevents a crystal of this type from disintegrating? Evidently very strong attractive and repulsive forces between neighboring atoms must be called into play. In many cases, such as that of sodium chloride, it has been demonstrated that these forces are largely due to the fact that *the atoms in the crystal lattice are not neutral, but electrically charged.*

How do the atoms obtain these electrical charges? This is where we begin to improve upon Dalton's original theory. As a result of recent progress in chemistry, we do not regard the atom any longer as the ultimate limit of divisibility; *the atom is itself divisible.* For each element, in fact, a definite atomic structure has been worked out which increases in complexity with the atomic weight. In general it is a very difficult matter indeed to pick an atom to pieces, but almost every species of atom contains, as its outermost shell, one or more *electrons,* or units of negative electricity (p. 63), which are relatively loosely held. Only these loose electrons are affected by ordinary chemical reactions, the rest of the atom stays intact. Atoms of metallic elements, as a rule, tend to relinquish their loose electrons; atoms of non-metals, on the other hand, generally prefer to acquire additional ones. Consequently, when so-

*** For the significance of the above figure, see footnote on p. 64.**

dium combines with chlorine to form sodium chloride, all that the combination actually involves is the transfer of one electron from each sodium atom to each chlorine atom. Each sodium atom, being originally *electrically neutral* (that is, containing just as many positive as negative units of electricity), and having *lost a negative charge,* is thereby converted into a positively-charged sodium atom Na^+ (or **sodium ion,** see p. 148), while each chlorine atom becomes a negatively-charged chlorine atom Cl^- (or **chloride ion**). The full significance of this transfer of electrical charges between the two constituent elements cannot be discussed here, but in later chapters (see particularly pp. 148, 298, 489) we shall repeatedly return to the question under various pretexts. Meanwhile it will suffice to

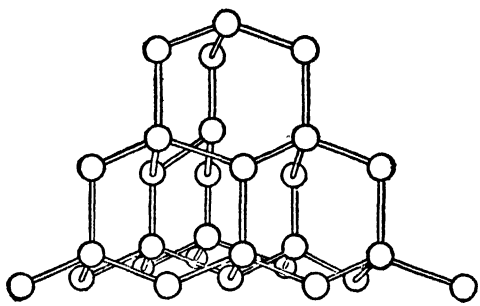


FIG. 38. Ultimate Structure of a Diamond.

mention that compounds of the type of sodium chloride, where combination is limited to a transfer of electrons, are called **polar.**

Other Lattice Types. — Most substances crystallize in less simple geometrical forms than the cube and consequently possess a rather more complex structure. The framework of the carbon atoms in a *diamond,* for example, is indicated in Fig. 38. The hexagonal lattice of a crystal of *magnesium* is shown in the lower diagram facing p. 67.

Coming to cases of compounds, the arrangement of the atoms in a crystal of *potassium hydrogen fluoride* is shown in Fig. 39; here we have two atoms of fluorine to each one of potassium and of hydrogen in the extended lattice. Portions of a unit in the grouping of a *tin tetra-iodide* crystal, finally, are shown in Fig. 40; here we have four atoms of iodine to each one of tin.

Molecules. — It has been emphasized, in an earlier stage of the discussion (p. 66), that the unit particles in the crystal lattice of a compound substance are single atoms, and not molecules. Nevertheless, in many crystals, particularly those of organic substances (p. 558), a definite "grouping" of atoms is recognizable. Thus in benzene, a compound of hydrogen and of carbon containing equal atomic quantities of the two constituent elements, we do not have any suggestion of similarity to the sodium chloride arrangement. Instead, we find the carbon and hydrogen atoms *arranged in distinct groups,* each group consisting of six carbon and six hydrogen

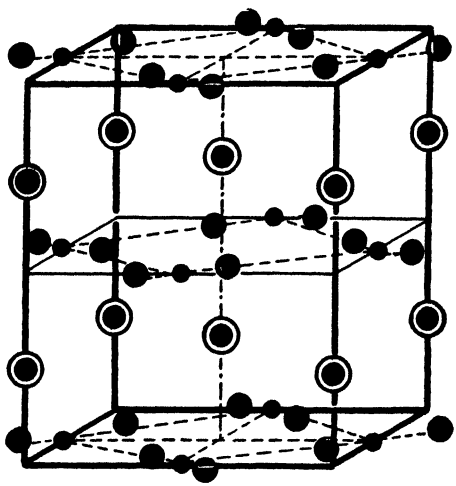


FIG. 39. Potassium Hydrogen Fluoride.
The ringed circles represent potassium atoms; the larger black circles fluorine atoms. The probable positions of the hydrogen atoms are indicated by the smaller black circles.

atoms. Similarly in naphthalene, another "hydrocarbon" (p. 577), we have groups containing ten carbon and eight hydrogen atoms. The same clustering is found in many inorganic crystals, such as sulphur and silica, and is indicated, indeed, in Fig. 40 for tin tetraiodide.

Substances of this type are termed **non-polar,** since they differ entirely in their chemical behavior from substances like sodium chloride, as we shall see later. The unit group of atoms within the crystal we call the **molecule,** and we find that when the substance is transformed, by change of conditions, into the liquid state (by fusion or solution), or into the vapor state (by sublimation, p. 350), these molecular units are still existent as definitely discrete groups.

The relative weight of such a group of atoms, consisting of the sum of the atomic weights of all of the atoms composing it, on the scale oxygen = 16, is a most important factor in chemical theory, as we shall develop in detail in a later chapter. It is called the **molecular weight.**

Two significant points remain to be mentioned in connection with this conception of discrete groupings of atoms, called molecules. One is that although the molecule, as such, is not actually existent in crystals of polar substances, such as sodium chloride, yet the study of the vapors of such substances at high temperatures shows that definite association of atoms can also occur in

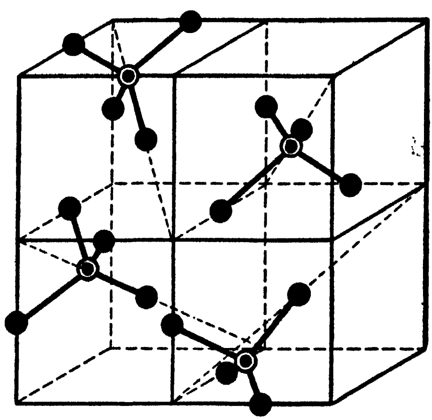


FIG. 40. Tin Tetra-iodide.

The ringed circles represent tin atoms; the black circles indicate the probable positions of the iodine atoms.

compounds of this class. In the vapor of sodium chloride, for example, we have molecular units of single sodium atoms in conjunction with single chlorine atoms. The molecule is potential, therefore, in the crystal, even if not real, and we commonly speak of the molecular weight of sodium chloride as represented by the sum of the atomic weight of sodium 23.00 and the atomic weight of chlorine 35.46, *i.e.*, 58.46, even although the term has no rigid significance except for the compound in the gaseous state.

The final point, a most important one, is that in many gaseous elementary substances, such as hydrogen, oxygen, nitrogen, and chlorine, the atoms of the element in the free state are always,

under ordinary conditions of temperature and pressure, associated in groups, and these groups also conform to the conception of molecules. Thus the molecule of gaseous hydrogen consists of two hydrogen atoms, and the molecular weight of hydrogen on the scale oxygen = 16 is 2.016. The molecule of oxygen also contains two atoms, and the molecular weight of oxygen is therefore twice its atomic weight, namely 32. The association of atoms is not always into groups of two, however. In the vapor of phosphorus at low temperatures we have units of four atoms, in the vapor of sulphur we have units of eight. In some elements, on the other hand, such as argon, the atoms are totally independent, and if we define the molecule as the smallest particle of a substance that exists in the gaseous state, then for such elements the terms "atom" and "molecule" are identical.

Methods for the determination of molecular weights will be described, and the fundamental importance of the concept duly emphasized, in a subsequent chapter (Chapter XI).

The Number of Atoms in the Gram-atomic Weight. — Having determined, by the study of the lattice structure of an element in the crystalline state, the type and dimensions along each axis of the fundamental pattern into which the individual atoms fall, and knowing also the density of the crystal, it is obviously a simple matter for us to calculate how many atoms are present in the space occupied by a gram-atomic weight of the element, and so to arrive at the actual weight of the atom itself in each particular case.

In crystals of metallic copper, for example, the atoms are arranged in a face-centered cubic lattice, illustrated in the model opposite p. 67. From the way in which the atoms are arranged and from the size of the unit cube, we discover that there are no fewer than 8.52×10^{22} atoms of copper in one cubic centimeter. Now, the density of copper is 8.93, that is, one cubic centimeter of copper weighs 8.93 grams. Therefore, there are 9.54×10^{21} atoms of copper in one gram! More significant still is the number of atoms in the *gram atomic weight* of copper, since this number should be the same for all elements if the chosen atomic weights are correct. The atomic weight of copper is 63.6, so that one gram atomic weight represents 6.06×10^{23} atoms. We obtain this same number by analyzing the crystal lattices of other elements, and it agrees also within error limits with values that had been deduced by chemists much earlier, but indirectly, with the assistance of the kinetic-

molecular hypothesis (see pp. 183, 185). Consequently, we feel quite certain that all the steps in our general argument are valid, and that the atomic weights which we have selected for the different elements (on the basis Oxygen = 16) are fully justified.

In conclusion, it must be understood that although we can, as demonstrated above, calculate the exact weight of single atoms, these ultimate particles of matter are far too minute to be observed directly. The number of zeros in the figures given in the preceding paragraph affords some idea as to the infinitesimal size of the individual atoms, but perhaps an illustration will make this point still more plain to the student. Imagine that a single gram of copper could be expanded to a scale where the single atoms would be as large as grains of sand (say 1 cubic millimeter). The mass of material so obtained would suffice to cover the whole area of the United States to a depth of about 4 feet!

Another striking illustration will be found in Exercise 7 below, and we shall return to the subject again in a different connection in Chapter XI.

Exercises. — 1. To raise the temperature of 1000 grams of an elementary substance in the solid state 1°, calories (p. 161) are required What is the approximate atomic weight of the substance?

2. We find by analysis that platinic chloride contains 48.8 parts of platinum combined with 35.46 parts of chlorine. The specific heat of platinum is 0.0324. What is its exact atomic weight?

3. 65.37 parts of zinc and 70.92 parts of chlorine are chemically equivalent quantities (p. 133). The specific heat of zinc is 0.093. What is its exact atomic weight?

4. Plot, on coördinate paper, *specific heat* against *atomic weight* for the following elements:

Element	Li	C	Na	P	K	Fe	Br	Ag	Au	I
Sp. Ht.	0.937	0.460	0.290	0.202	0.166	0.112	0.084	0.054	0.031	0.0

Draw a smooth curve through your results. What is the equation for t curve? Read off, from the curve, the predicted specific heats for the foll ing elements: Mg, Ca, Zn, Sr, Cd, Ba, Hg.

5. What connection is there between the atomic theory and (*a*) the of definite proportions, (*b*) the law of multiple proportions?

6. Why should the number of atoms in the gram-atomic weight be same for all elements?

7. There are 50 billion atoms of gold in a drop of sea-water! Assumin that 30 drops of sea-water weigh a gram, calculate the weight of gold present in a metric ton (1000 kg.) of the ocean.

8. The density of rock salt at 20° is 2.17. What is the *exact* distance between the centers of adjacent atoms in its crystal lattice (see p. 69)?

READING REFERENCES

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CHAPTER V

SYMBOLS, FORMULÆ AND EQUATIONS

Having developed in outline the ideas of combining proportions and atomic weights, we are now in a position to indicate the important practical applications of these ideas in chemistry.

A consideration of the contents of the foregoing chapters will show that the complete description of a chemical change may be exceedingly involved. In a moderately complex action, such as that of sodium chloride upon silver nitrate (p. 31), we should have to say that sodium chloride, composed of one atomic weight each of sodium and chlorine, when brought in contact with silver nitrate, composed of one atomic weight each of silver and nitrogen and three atomic weights of oxygen, *gave* silver chloride, composed of one atomic weight each of silver and chlorine, and sodium nitrate, composed of one atomic weight each of sodium and nitrogen and three atomic weights of oxygen. Such a statement, while it would give all the facts in the quantitative point of view, would be difficult to grasp and lacking in clearness.

Symbols and Formulæ. — In order to represent the nature of a chemical change in a form which may be taken in at a glance, the chemist is in the habit of using certain **symbols,** first introduced by Berzelius. Thus, the letters Ag represent one atomic weight (*i.e.*, 107.88 parts) of silver (*argentum*), and O represents one atomic weight (*i.e.*, 16 parts) of oxygen. In other words, the **symbol** of an element **means one chemical unit weight (atomic weight) of the element.** Since the names of many elements begin with the same initial, two letters have frequently to be used to distinguish them. Thus, C stands for one atomic weight (12 parts) of carbon, Ca for one atomic weight (40.07 parts) of calcium, Cl for 35.46 parts of chlorine. When the names of the elements are not the same in all languages, resort is frequently had to Latin. Thus, Cu stands for one weight of copper (*cuprum*), Fe is used for iron (*ferrum*), Hg for mercury (*hydrargyrum*). From German we have Na for sodium

(*natrium*) and K for potassium (*kalium*). These symbols are international, and a list of them is included in the table of atomic weights printed inside the back cover of this book (see also pp. 446, 475).

The composition of any compound can thus be stated by setting down the necessary symbols, together with the whole numbers, if different from unity, by which the atomic weights are multiplied.

Thus, sodium chloride is represented by the symbols NaCl (= 23 of sodium to 35.46 of chlorine), silver nitrate by the symbols $AgNO_3$ (= 107.88 of silver, 14.01 of nitrogen, and 3 × 16 of oxygen). Such a combination of symbols is called a **formula.** For example, magnetic oxide of iron contains iron 167.52 and oxygen 64 parts (p. 53). This is equivalent to iron 3 × 55.84 and oxygen 4 × 16. This again is equivalent, in symbols, to 3 × Fe and 4 × O. The formula is written Fe_3O_4. Ferrous sulphide is a simpler case: iron 55.84 and sulphur 32.06, or, in symbols, FeS. The reader should now examine the condensed statements of various reactions included in the preceding chapters, and work out the formula of each compound and write it in the margin.

It must be noted particularly that the *formula*, to be consistent, *must represent also the total weight of the unit quantity of the substance in the gaseous state, i.e.*, the **molecular weight** (p. 72). Thus, HCl (1.008 + 35.46 = 36.468) is correct, since the molecule of HCl in the gaseous state contains one atom of hydrogen and one of chlorine. However, the formula for oxygen itself must represent the association of two atoms of oxygen in the molecule, and is therefore O_2. Half as much as this may enter into a compound, H_2O, ZnO, etc., but logically, the formula for free oxygen must record the double weight when the gas is present alone, in the free condition (see pp. 70, 189). Similarly the formula for hydrogen is H_2, and for benzene (p. 71) C_6H_6. *The formula of every volatile substance must thus be written so as to show the weight of the chemical unit quantity, the molecular weight.* When the substance is not easily volatilized, this unit cannot be directly measured, and in default of any information derived by indirect methods (see pp. 212–7) the simplest formula is employed.

Information Contained in Each Formula. — A formula thus contains, in condensed form, several items of information. It shows:

1. The elements making up the substance,
2. The proportion by weight of these elements,

3. The total unit weight (molecular weight) of the substance. Given the formula, we can read these facts in it.

Thus, if we are given the formula of carbon dioxide, CO_2, we consult the table of atomic weights (inside rear cover), and learn that $C = 12.00$ *parts* by weight of *carbon* and $O_2 = 2 \times 16$ parts by weight of *oxygen*. The proportion by weight of the elements in this compound is, therefore, 12.00 of carbon to 32 of oxygen. The total weight (molecular weight) is $12.00 + 32 = 44.00$.

Derivation of Formulæ from Experimental Data. — In the condensed statements presented in previous chapters, the numbers included were already multiples of the atomic weights, and the formulæ were therefore easy to make. It remains to show how the formula may be constructed from the weights obtained in an experiment.

In the quantitative experiment on the composition of cupric oxide (p. 44), the proportion found was: copper 85, oxygen 21. In the formula, the same proportion is to be expressed by means of multiples of the atomic weights. If we divide each of these numbers by the corresponding atomic weight, the quotient will be the number by which the atomic weight must be multiplied. The atomic weights are $Cu = 63.57$, $O = 16$. Now $85 \div 63.57 = 1.3$, and $21 \div 16 = 1.3$. The proportion of copper to oxygen in the compound, $\frac{85}{21}$, thus becomes $\frac{63.57 \times 1.3}{16 \times 1.3}$.

But this proportion must be expressed in multiples of the atomic weights by *whole* numbers. Dividing above and below by 1.3, we get $\frac{63.57 \times 1}{16 \times 1}$.

Now the symbols stand for the atomic weights. Substituting the symbols, the proportion becomes $\frac{Cu \times 1}{O \times 1}$. The formula is, therefore, CuO.

Applying the same process to the case of tin oxide (p. 16):

$$\frac{\text{Tin}}{\text{Oxygen}} = \frac{100}{26.9} = \frac{118.7 \times 0.84}{16 \times 1.68} = \frac{118.7 \times 1}{16 \times 2} = \frac{Sn \times 1}{O \times 2}, \text{ or } SnO_2.$$

If the composition of the substance has been stated in percentages,

the same device is used. Thus, the case of sodium sulphate works out as follows:

Elements	Percentages	At. Wt.		Quotient	÷	Formula
Sodium....................	32.43	23	×	1.41	0.705	Na × 2
Sulphur....................	22.55	32	×	0.705	0.705	S
Oxygen....................	45.02	16	×	2.814	0.705	O × 4

The formula is, therefore, Na_2SO_4.

Formulæ obtained by this arithmetical method are known as **empirical formulæ.** They give us the correct atomic proportions of the constituent elements, expressed in the lowest possible whole number ratios. In many cases, however, it is necessary to multiply the empirical formula of a substance throughout by 2, or 3, or some other whole number greater than 1, in order to arrive at the true **molecular formula.** Some examples will be discussed in a later section (p. 191).

An Alternative Method. — If the molecular weight of the substance is given (*not otherwise!*) a simpler alternative method is available. Let us illustrate this also by an example.

The mol. wt. of cyanogen is 52.02. Its percentage composition is found to be carbon 46.08, nitrogen 53.92. What is its formula?

Since 46.08 per cent of the substance is carbon, 1 g. mol. wt. contains $52.02 \times 46.08/100$ g. = 23.97 g. of carbon. But 1 g. atomic wt. of carbon = 12.00 g. Therefore 1 mol. wt. of the substance contains 23.97/12.00, or (within error limits) 2 atomic wts. of carbon. Each molecule consequently contains two carbon atoms.

Similarly, since 53.92 per cent of the substance is nitrogen, 1 g. mol. wt. contains $52.02 \times 53.92/100$ g. = 28.04 g. of nitrogen. But 1 g. atomic wt. of nitrogen = 14.008 g. Therefore 1 mol. wt. of the substance contains 28.04/14.008, substantially 2 atomic wts. of nitrogen. Each molecule consequently contains two nitrogen atoms.

The molecular formula of cyanogen is therefore C_2N_2.

Equations. — It is now possible to abbreviate the condensed statements we have been using to represent the substances and their quantities in chemical reactions. Thus, the third statement on p. 17:

$$\text{Iron } (4 \times 55.84) + \text{Oxygen } (3 \times 32) \rightarrow \text{Ferric Oxide } (319.36)$$

when translated into symbols, reads as follows:

$$4Fe + 3O_2 \rightarrow 2Fe_2O_3.$$

This expression contains all that was conveyed by the words which were written out in full. Such "shorthand" expressions are called **equations.**

The object in writing a series of formulæ in the above manner is to show that the system upon the left-hand side, consisting of certain substances whose composition and properties we know, is, under the conditions of the experiment, unstable, and changes into the system upon the right-hand side, whose nature we also know. The materials on the two sides are essentially different, for the transformation represented is a chemical *change*. It is somewhat anomalous, therefore, that, to connect two sets of things which are essentially different, the sign = is usually employed. To call this a *chemical* equation is still more anomalous, since it is precisely in the chemical point of view that the difference between the two sides is most strongly to be emphasized. It represents two sets of things which are different, and not alike chemically. The physical properties of the two sets of substances are likewise totally unlike. There is only one respect in which the materials on the two sides agree, and that is that their mass is not different. This is, however, merely an example of the law of conservation of matter, and need not, therefore, be specially commemorated in the form in which we write every equation. Above all it must be remembered that the chemical equation is not an algebraic expression; it is not subject to the rules of algebra. It is a brief expression, in terms of the atomic weights, of the distribution in kind and quantity of the constituents of a system before and after chemical change.

Writing Equations. — *In making an equation* there are **four stages or steps:**

1. Find out by experiment what the substances used and produced are.
2. Learn the molecular formula of each substance.
3. Set down the molecular formulæ in the form of a skeleton equation. Place the formulæ of the *initial substances* on the *left,* and those of the products on the right.
4. Adjust, or *balance* the equation.

For example:

(1) When hydrogen and oxygen combine, water is formed.

(2) The molecular formulæ are H_2, O_2, and H_2O.

(3) Skeleton equation: $H_2 + O_2 \rightarrow H_2O$.

(4) In accordance with the law of conservation of mass, the numbers of atomic weights (or atoms) of each element must be the same after the action as before it. Now the skeleton equation shows two atomic weights of oxygen before, and, thus far only one after the action, whereas there ought to be two there also. With O_2 (2×16 parts) we have enough oxygen to give $2H_2O$, which contains 2×16

parts of oxygen. But this will require us to take $2H_2$ to "balance" the equation. The final equation is, therefore:

Balanced Equation: $2H_2 + O_2 \rightarrow 2H_2O$.

Observe, we could not adjust the difficulty by writing $H_2 + O \rightarrow H_2O$, because each substance must be represented by its *molecular* formula, and in the case of oxygen this is O_2 (= 32 g.). Putting this in terms of atoms and molecules, each formula must represent 1 molecule, and the molecules of oxygen contain 2 atoms. Now we could not take less than one oxygen molecule. But we *could take more than one molecule* of hydrogen, so we took 2 molecules of this substance.

The coefficients in front of formulæ multiply the *whole* formula. $2H_2O$ is equivalent to $2(H_2O)$, or two whole molecules of water.

Balancing Equations.— Learning to balance equations correctly comes only by practice. Take, again, the case of iron rusting. The substances are iron (Fe), oxygen (O_2) and ferric oxide (Fe_2O_3). The skeleton equation is:

$$Fe + O_2 \rightarrow Fe_2O_3.$$

We are not permitted to alter these formulæ themselves, but we may put coefficients in front of any of them to make the number of atomic weights alike on both sides. A good rule is to *pick out the largest formula and reason back from that.* Here, this is Fe_2O_3. To get oxygen atoms in *threes,* we must clearly take $\mathbf{3O_2(=60)}$. That will give us $\mathbf{2Fe_2O_3}$. This, in turn, will require **4Fe:**

Balanced: $\mathbf{4Fe + 3O_2 \rightarrow 2Fe_2O_3}$.

The student should endeavor to obtain all possible experience in writing and balancing equations by turning back to the condensed statements of chemical changes in earlier chapters, obtaining the necessary atomic weights and symbols from the table at the end of the book, and constructing the equation in each case.

Study carefully the rules given for making and balancing equations (p. 80). **Do not think that because an equation balances on paper, it is necessarily correct.** The substances that you have written on the right-hand side may not be obtainable from those on the left under any experimental conditions. *You have got to know what the products of a reaction are before you can begin to balance your equation.*

Calculations

As we have seen (p. 77), the formula represents the composition of a substance, using the atomic weights as the units. We have learned how the formula is calculated from measurements made in an experiment (p. 78). We may now take up some of the ways of using the information contained in a formula.

Composition from the Formula. — To learn the composition of a substance, such as potassium chlorate $KClO_3$ (see p. 91), from its formula, we look up the values of the atomic weights (inside rear cover). We find K = 39.1 parts of potassium, Cl = 35.46 parts of chlorine, and $O_3 = 3 \times 16$ or 48 parts of oxygen. The proportions, in order, are therefore: 39.1 : 35.46 : 48.

To find the percentage composition, we proceed as follows. In potassium chlorate the proportions are 39.1 of potassium, 35.46 of chlorine, and 48 of oxygen — a total of 122.56. In one hundred parts, the potassium is $\frac{39.1}{122.56} \times 100$, or 31.9; the chlorine $\frac{35.46}{122.56} \times 100$, or 28.9; and the oxygen $\frac{48}{122.56} \times 100$, or 39.1.

Stated in terms of the rule of proportion, we have, for the potassium, $122.56 : 39.1 :: 100 : x$, where x is the percentage of potassium.

Calculations by Use of Equations. — We frequently wish to know what weight of a product can be obtained from a given weight of the necessary materials, or how much material is required to furnish the desired weight of a product. For example, what weight of ferrous sulphide can be made with 100 g. of iron? It is understood, of course, that the necessary sulphur is available.

To avoid the blunders which are easily made, observe strictly the following rules:

1. **Write down the equation:**

$$Fe + S \rightarrow FeS.$$

2. **Place under each formula the weight it represents:**

$$\begin{matrix} Fe & + & S & \rightarrow & FeS \\ 55.84 & & 32.06 & & 87.90 \end{matrix}$$

3. **Read this expanded equation:** In this case it reads: 55.84 parts of iron combine with 32.06 parts of sulphur to give 87.90 parts of ferrous sulphide.

4. **Re-read the original problem:** "What weight of ferrous sulphide can be made with 100 g. of iron?" Having done this, place the amount given in the problem (100 g. of iron) under the formula of the substance in question. Then notice what the problem asks ("what weight of ferrous sulphide") and place an x under the formula of that substance:

$$\begin{array}{ccccc} \text{Fe} & + & \text{S} & \rightarrow & \text{FeS} \\ 55.84 & & 32.06 & & 87.90 \\ 100\text{ g.} & & & & x \end{array}$$

5. **Read the problem as now tabulated:** 55.84 g. of iron give 87.90 g. of ferrous sulphide, therefore 100 g. of iron will give x g. of ferrous sulphide.

6. **State the proportion in this order** (or, see below):

$$55.84 : 87.90 :: 100 : x \ (= 157.4 \text{ g.}).$$

If the tabulation in rule 4 has been prepared correctly, this final statement as a proportion is purely mechanical. It will be noted that only two of the three quantities given in the expanded equation were actually used.

6a. **Alternative Method.** At the sixth step, we may also say: If 55.84 g. of iron give 87.90 g. of ferrous sulphide, 1 g. of iron will give $\frac{87.90}{55.84}$ g. ($= 1.574$ g.) of ferrous sulphide. Then, if 1 g. of iron gives 1.574 g. of ferrous sulphide, the 100 g. of iron will give 100×1.574 g. ($= 157.4$ g.) of ferrous sulphide.

Warnings. — In solving the exercises at the end of the chapter, beware of *three kinds of mistakes* commonly made by beginners.

1. Conquer a tendency to say that the symbols Fe and S stand for "1 part" of iron or of sulphur. They stand for 1 *chemical unit,* or atomic weight, or atom, in each case, — that is to say, for 55.84 "parts" and 32.06 "parts," respectively.

2. Follow the rules laid down above. When you have once *become familiar* with the art of solving such problems, running through the rules takes only a few seconds. The chemist does it almost unconsciously. The beginner *always* thinks he can ignore these rules, and he fails in consequence. Writing the

equation in the expanded form, and then reading the problem into it, are absolutely essential steps.

3. Do not read the original problem carelessly and make the equation *backwards*, that is with the sides reversed. If there seems to be confusion somewhere, when the last steps are reached, this hint will probably show the cause of the difficulty.

Exercises. — 1. From the data on p. 16 and the atomic weights, calculate the formula of lead oxide.

2. When 1 g. of sodium burns in oxygen, it produces 1.7 g. of the oxide. What is the empirical formula of the latter? Reconcile with p. 93.

3. If 26 g. of mercurous oxide are required to give, by heating, 1 g. of oxygen, what is the formula of the substance?

4. What are the empirical formulæ of the substances possessing the following percentage compositions?

I		II		III	
Magnesium	25.57	Sodium	36.49	Potassium	26.585
Chlorine	74.43	Sulphur	25.43	Chromium	35.390
		Oxygen	38.08	Oxygen	38.025

5. What are the percentage compositions of substances possessing the following formulæ: Mn_3O_4, KBr, $FeSO_4$?

6. What weight of mercury is obtained from 120 g. of mercuric oxide HgO?

7. What weight of mercuric oxide will furnish 20 g. of oxygen?

8. What weight of Fe_2O_3 may be obtained from 10 g. of oxygen?

9. How much silver is contained in 100 g. of an impure specimen of silver chloride AgCl which is 33 per cent sand?

10. What are the percentage compositions of cerium sulphate $Ce(SO_4)_2$, phosphorus pentachloride PCl_5, and ammonium chloride NH_4Cl?

11. What weight of hydrogen is required to reduce 100 g. of ferric chloride $FeCl_3$ to ferrous chloride $FeCl_2$?

12. Gypsum is a compound of water and calcium sulphate ($CaSO_4$). If 6 g. of gypsum, when heated, lose 1.256 g. of water, what is the formula of the compound?

13. What weight of oxygen would be required to burn 100 g. of benzene (C_6H_6) to carbon dioxide (CO_2) and water?

14. What weight of oxygen would be liberated by the conversion of 50 g. of manganese dioxide MnO_2 to hausmannite Mn_3O_4?

15. What are the empirical formulæ of the substances possessing the following percentage compositions?

I		II		III	
Calcium	38.72	Carbon	77.34	Carbon	71.96
Phosphorus	20.00	Hydrogen	7.58	Hydrogen	6.72
Oxygen	41.28	Nitrogen	15.08	Oxygen	21.32

16. Given the percentage composition of nitrobenzene: Carbon, 58.53, Hydrogen 4.07, Nitrogen 11.39, Oxygen 26.01; calculate its empirical formula.

17. The molecular weight of naphthalene is 128.18. It contains 93.66 per cent of carbon, and 6.34 per cent of hydrogen. What is its molecular formula?

READING REFERENCE

Hauben; The Derivations of the Names of the Elements. Journal of Chemical Education, 10, 227, 1933.

CHAPTER VI

OXYGEN

We begin the more systematic study of chemistry with oxygen, for it is a most interesting as well as useful substance. It is the active component in the air. We depend upon it for *life*, since in its absence we suffocate, for *heat*, since wood, coal, and gas will not burn without it, and even for *light* where oil, gas, or a candle is employed.

We wish to know with which substances we use in the laboratory it can combine, as well as the substances on which it has no action. This information will show us how to work, in future, without interference from the oxygen in the air and whether oxygen has probably played a part in some experiment or not.

We take up, then, (1) the **history** of the element, (2) what materials contain oxygen (**occurrence**), (3) how we can obtain it in a pure state (**preparation**), (4) what its **specific physical properties** as a substance are, and (5) what it does, and what it can not do in nature and in the laboratory (**chemical properties**). The classification of the facts about this, and other substances, under five heads is somewhat mechanical, but has the advantage of enabling the reader quickly to find any required information.

To these five heads the student may add with advantage a sixth, namely **uses.** This will correlate the first five automatically, and at the same time keep the subject alive to him by emphasizing its importance outside of the laboratory. A substance is drafted into the service of man sometimes because of a **physical property,** sometimes because of a **chemical property.** How widely it can be employed depends upon the abundance and availability of its **sources**, and upon the ease of its **preparation** and its **purification.** These are the very points which have influenced, very largely, **pioneer research work** upon the substance. If we know the uses of a substance, therefore, and *understand exactly why* it is applicable to each particular use, we shall automatically make ourselves familiar with the chemistry of that substance.

Specific Properties of Two Kinds, Physical and Chemical. — We have learned that every substance has its own set of specific properties. In de-

scribing a substance, it is convenient to divide the properties into two classes. The list of substances with which the given substance can enter into chemical combination, for example, we place under **specific chemical properties.** Reactions of the substance involving any of the varieties of chemical change (p. 232) belong to this class.

On the other hand, we do not consider melting or boiling to be chemical changes, so we place the temperatures at which the substance melts (m.-p.) and boils (b.-p.), its color, etc. (for list, see p. 9) under **specific physical properties.**

Properties of either class may be used for recognizing a substance.

History of Oxygen. — While many elements which are less easily obtainable than oxygen have been recognized as distinct substances for many centuries, oxygen did not attain this position until the end of the eighteenth century. The reason for this was that gases are not so easy to handle and distinguish as are solids or liquids, and consequently very slow progress was made in the study of them.

Leonardo da Vinci (1452–1519) seems to have been the first European to mention the presence of two different gases in atmospheric air. Mayow (1669) measured the proportion of oxygen in the air and discussed fully its uses in combustion, rusting, vinegar-making, and respiration, but did not make a pure sample. Hales (1731) made it by heating saltpeter, and measured the amount obtainable, but did not see any connection between it and the air. Bayen (April, 1774) was the first to make it by heating mercuric oxide. Priestley (an English nonconformist minister who occupied his leisure time with experiments in chemistry) was particularly interested in examining the nature of the gases which were evolved by some materials when heated. His plan was to fill an elongated glass vessel with mercury, to invert this in a trough filled with the same metal, and, after allowing the substance under examination to float up into the top of the tube above the mercury, to expose it to the rays of the sun concentrated by a large burning lens (Fig. 41). Priestley found (Aug. 1, 1774) that one material, then known as *"mercurius calcinatus per se"* (mercuric oxide), gave off an unusual amount of gas. Quite purposelessly, as he admits, he thrust a lighted candle into it and was delighted with the extreme brilliance of the flame. He had, however, no notion until a year later that it was a component of the air. Even then, he thought it was a compound of nitric acid, earth,

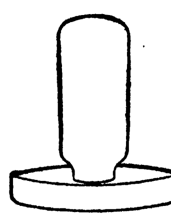


FIG. 41. Priestley's Apparatus.

and phlogiston! Scheele, a Swedish apothecary, had made it in 1771–2 from no less than seven different substances and understood clearly that atmospheric oxygen combined with metals, phosphorus, hydrogen, linseed oil, and many other substances. But his book was not published until 1777, and Priestley is usually credited with the "discovery" of the element.

Lavoisier at first (1773–5) thought that air was composed of nitrogen and "fixed air" (carbon dioxide). Although Priestley had dined with him (Oct., 1774), and communicated his discovery, so far as he understood it himself, yet when Lavoisier heated mercuric oxide in March, 1775, he expected to obtain "fixed air." Later in the same year, Lavoisier held that air contained no "fixed air," and was made up of a single gas. It was not until 1777 that he heated the metal mercury in a retort (Fig. 42), the neck of which projected into a bell-jar standing in a larger dish of mercury. The air, thus enclosed within the jar and the retort, during twelve days lost one-fifth of its volume. Simultaneously, red particles of mercuric oxide accumulated on the surface of the mercury in the retort. The residual gas no longer supported life or combustion, and hence was named by Lavoisier "azote" (Greek, ἀ, without, and ζωή, life). In English it is called nitrogen. The oxide, on being heated more strongly by itself, gave off a gas, the volume of which exactly corresponded with the shrinkage undergone by the enclosed air, and this gas possessed in an exaggerated degree the properties which the air had lost. The proof that oxygen was a component of the atmosphere was therefore complete. Lavoisier, in the mistaken belief that the new element was an essential constituent of all sour substances, named it **oxygen,** or acid-producer (Greek, ὀξύς, an acid, γεννᾶν, to produce). Cavendish pointed out almost immediately that there were sour-tasting substances which contained no oxygen, so that the name has no longer any significance. It may here be noted that *hydrogen* is the only element which is found in all acids.

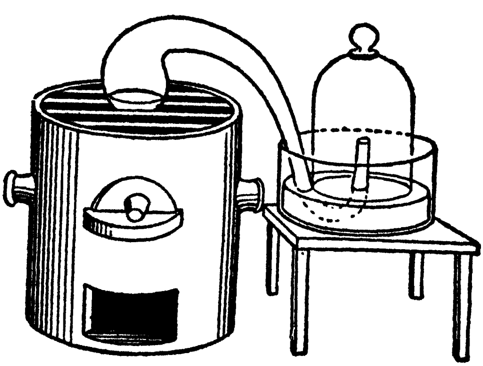


FIG. 42. Lavoisier's Apparatus.

Occurrence. — As we have seen (p. 28), nearly 50 per cent of terrestrial matter is oxygen. Water contains about 89 per cent, the human body over 60 per cent, and common materials like sandstone, limestone, brick, and mortar more than 50 per cent of this element in combination. Approximately one-fifth by volume (nearly one-fourth by weight) of the air is *free* oxygen.

Preparation of Oxygen. — 1. The oxygen of commerce is now made chiefly from **liquefied air** (p. 460). This consists essentially of a mixture of liquid oxygen and liquid nitrogen. Now pure liquid oxygen boils at — 182.5°, but pure liquid nitrogen boils at an even lower temperature (— 196°). Consequently, when liquid air is allowed to evaporate slowly, the nitrogen boils off much more freely than does the oxygen. After a time, when the remaining liquid is almost pure oxygen (96 per cent), the gas coming off is compressed by pumps into the steel cylinders in which it is sold.* In medicine, patients suffering from pneumonia or suffocation obtain some relief by inhaling it in this form. It is also used in feeding flames, instead of air, when intense heat is required (see pp. 139 and 586).

2. Unfortunately, it is difficult to liberate oxygen from **natural substances.** Saltpeter (potassium nitrate KNO_3), for example, which is found in many soils and can be dissolved out with water, gives off oxygen only when raised to a bright red heat by the Bunsen flame or blast lamp, and even then it gives up only one-third of the oxygen it contains, leaving potassium nitrite KNO_2:

$$2KNO_3 \rightarrow 2KNO_2 + O_2.$$

The mineral pyrolusite (manganese dioxide MnO_2), employed by Scheele, requires a still higher temperature to effect its decomposition. Again only one-third of the total oxygen present in the compounds is evolved, and an oxide of the composition Mn_3O_4 remains:

Skeleton: $$MnO_2 \rightarrow Mn_3O_4 + O_2.$$
Balanced: $$3MnO_2 \rightarrow Mn_3O_4 + O_2.$$

The liberation of oxygen from water by means of electrolysis (passing an electric current through water to which a substance such as

* This is the simplest method, but very wasteful. Some modern refinements of apparatus are discussed on p. 462.

sulphuric acid H_2SO_4 or sodium hydroxide NaOH has been added to make the liquid conduct) is a feasible laboratory method of preparation, but is not used commercially except in connection with the manufacture of hydrogen, where large quantities of oxygen are obtained as a by-product. The details of the reaction: $2H_2O \rightarrow 2H_2 + O_2$ will not, therefore, be taken up until we reach the preparation of hydrogen (p. 134).

3. In laboratory practice, we are generally compelled to use **manufactured substances.** Amongst these are mercuric oxide, expensive, but historically interesting (p. 23); barium peroxide, formerly used in manufacturing oxygen on a large scale (Brin's process); potassium chlorate, the most convenient for laboratory use; and sodium peroxide.

Brin's Oxygen Process. — Barium oxide BaO closely resembles quicklime CaO (p. 24), but differs from this substance in the fact that, when heated in air to about 500°, it rapidly acquires additional oxygen and gives barium peroxide BaO_2. When barium peroxide is raised to 1000°, this extra oxygen is given up again. Barium oxide contains one chemical unit weight each of the two constituents and takes up another unit of oxygen, so that the equation for the primary action is:

$$2BaO + O_2 \rightarrow 2BaO_2.$$

The subsequent decomposition of the peroxide, during the stage in which the oxygen is made, is the exact opposite: $2BaO_2 \rightarrow 2BaO + O_2$. The commercial advantage of the method lay in the fact that the barium oxide, remaining after the second stage, can be used over and over again. This, as will be seen, was in reality a chemical method of obtaining oxygen from the air.

In practice an improvement on the above principle made working more economical. It was found that if the barium oxide is maintained at a temperature of 700°, intermediate between the two just mentioned, oxygen is absorbed when air is forced under pressure into the tubes containing the oxide. A valve at the extremity of the tubes permits the escape of the nitrogen. When the combination with oxygen is completed, the pumping apparatus is reversed and, a partial vacuum being created, the oxygen in combination is given off without any alteration in temperature being necessary. Thus a great waste of fuel is avoided, and the process is rendered more nearly continuous.

Oxygen from Potassium Chlorate. — Potassium chlorate, $KClO_3$, is a white crystalline substance used in large quantities in the manufacture of matches and fireworks. When heated in a crucible like that in Fig. 5, it first melts (368°) and then, on being more strongly heated, it effervesces and gives off a very large volume of oxygen. The white material which finally remains after continued heating is potassium chloride KCl:

$$2KClO_3 \rightarrow 2KCl + 3O_2.$$

A peculiarity of this action is that admixture of manganese dioxide increases very markedly the speed with which the decomposition of the potassium chlorate takes place. Hence, in its presence, and it is generally mixed with the chlorate in the laboratory

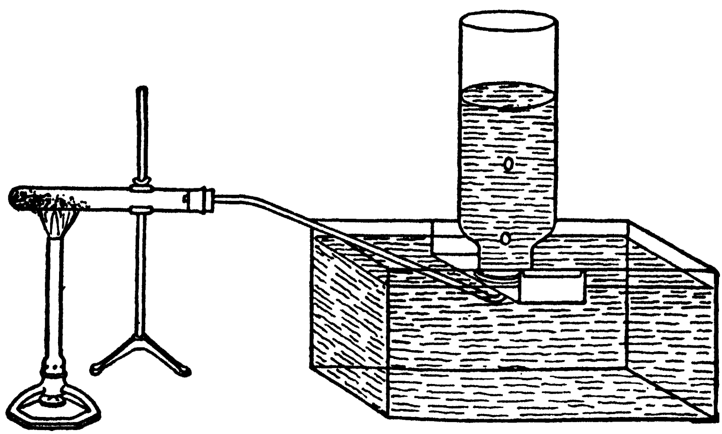


FIG. 43. Oxygen from Potassium Chlorate.

experiments, where the oxygen is collected over water (Fig. 43), a sufficient stream of gas is obtained at a relatively low temperature (below 200°, see p. 103). Hales (p. 87) was the first to collect a gas over water, in order that it might be kept unmixed with air.

Familiarity with Physics Required in the Study of Chemistry. — In mentioning chemical phenomena, it is inevitable that considerations of space should

limit our statements to the merest indication of the process and the briefest record of the chemical result. The prodigious disproportion between the meagerness of this fragment and the mass of detail which lies behind it in each case should be constantly before the mind of the reader. The book gives empirical knowledge, the laboratory work and the discussion of it furnish the only real knowledge. The extent and nature of this real knowledge may be shown in connection with any action. As an illustration we may point out some of the problems which the heating of potassium chlorate presents to one who is trying to acquire an intelligent acquaintanceship with its chemistry, and has not previously done the experiment.

First, the substance melts. It must be realized that this is a common occurrence which does not necessarily imply any profound change, and may be reversed by cooling. Later, the liquid appears to boil, and the properties of a boiling substance must be known. If the observer has been informed in advance that the body is homogeneous, he must know that, if it is simply boiling, it will evaporate completely and leave nothing behind, and that the temperature required to achieve this will remain constant from the beginning to the end. In order, therefore, to become aware of the fact that here decomposition is taking place, he must note the ways in which the decomposition of potassium chlorate differs from ordinary boiling. For example, if it were a case of boiling, he should expect to find the solid body condensing on the sides of the vessel, and note the fact that no such condensation is observed, with the appropriate inferences. He should observe that, in the later stages at least, the escape of the gas does not cease when the flame is removed, although this would undoubtedly occur in a case of simple boiling. He must further observe the changes in the consistency of the material and the way in which it finally becomes thick and may even solidify. Even the most experienced investigator would have to make many careful experiments before he could definitely classify the nature of the phenomenon being observed. The first inference would probably be that the phenomenon was certainly not one of mere ebullition. In some ways it is like the evaporation of a solution, obtained, say, by the melting of a substance like calcium chloride hexahydrate (see p. 213) in its so-called water of crystallization. Yet, this hypothesis would not explain to the thoughtful observer even the more obvious features of the phenomenon, for the liquid which was acting as a solvent would have to be amazingly volatile if the absence of any condensation on the walls of the vessel was to be accounted for.

The illustration need not be elaborated further. These remarks are sufficient to show that even the simplest experiment presents an almost limitless field for the discussion of important questions which are more or less common to all chemical phenomena. It must be noted, also, that chemical change is in itself not perceptible by the senses, and that only physical properties and physical phenomena are observed (compare pp. 35–7). The chemical facts, such as the general nature of the change, the conditions under which, and the facility with which it occurs, are reached solely by inference. The above example shows the ready and thorough knowledge of physics which must be at the command of every individual effort to study even the simplest chemical phenomenon. It is only when the physics as well as the chemistry of the change have been mastered that the "real knowledge" to which reference was made above has been gained.

Oxygen from Sodium Peroxide. — Oxygen can be obtained conveniently from sodium peroxide Na_2O_2 and water H_2O by means of generators (Fig. 44) similar to the acetylene generators used on bicycle lamps. When the metal sodium is burned in air, sodium peroxide is obtained as a powder. This powder, after being melted, solidifies in compact, solid form, and is sold as "oxone." The oxone is bought in a small, sealed tin can, the ends of which are perforated in several places just before use. When the valve (*B*) is opened, the water, which fills the generator almost to the top, enters the can (*C*) by the holes in the bottom and interacts with the oxone, forming sodium hydroxide NaOH and oxygen. The sodium hydroxide produced is very soluble in water and remains dissolved; the oxygen escapes through the valve. When the valve is shut, the gas continues to be generated until it has driven the water down again below the level of the bottom of the can, whereupon the reaction ceases.

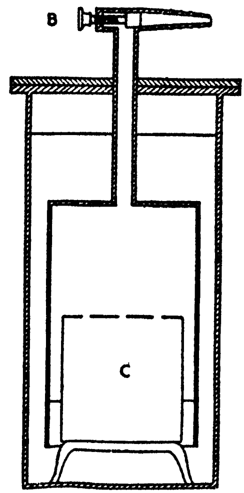


FIG. 44. Oxygen Generator.

Skeleton: $Na_2O_2 + H_2O \rightarrow NaOH + O_2$.
Balanced: $2Na_2O_2 + 2H_2O \rightarrow 4NaOH + O_2$.

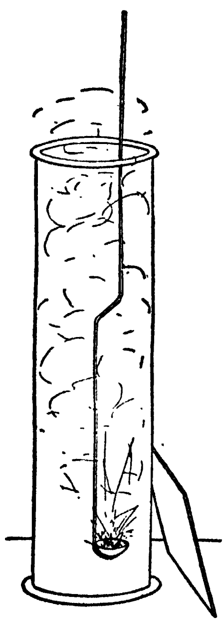
This method for the preparation of oxygen is convenient because it works at room temperature and can be started and stopped at will.

Specific Physical Properties of Oxygen. — Oxygen resembles air in having neither *color, taste,* nor *odor.* The *density* of a substance is, strictly speaking, the weight in grams of 1 cubic centimeter. In the case of a gas, we frequently prefer to give the weight of 1000 c.c. (1 liter), at 0° and 760 mm. (1 atmosphere) barometric pressure. For oxygen this weight is 1.42900 grams (Morley). The corresponding weight for air is 1.293 g., so that oxygen is slightly heavier, bulk for bulk, than air (in the ratio 1.105 : 1). It is much heavier than hydrogen, however, since one liter of this gas under the above conditions weighs only 0.08987 gram. Oxygen can be *liquefied* by compression, provided its temperature is first reduced below —118°, which is its critical tem-

perature.* The gas is only slightly *soluble* in *water* under atmospheric pressure, the solubility at 0° being 4.9 volumes of gas in 100 volumes of water (at 20°, 3.1 : 100).

The solubility of oxygen in water, although slight, is in some respects its most important physical property. Fish obtain oxygen for their blood from that *dissolved in* the water. With air-breathing animals (like man), the oxygen could not be so readily taken into the system, if it did not first dissolve in the moisture contained in the walls of the air sacs of the lungs, and then pass inwards in a dissolved state to the blood.

Liquid oxygen, first prepared by Wroblevski, has a pale-blue color. At one atmosphere pressure, that is, in an open vessel, it boils at — 182.5°. Its density (weight of 1 c.c.) is 1.13, so that it is slightly denser than water. By cooling with a jet of liquid hydrogen, Dewar froze the liquid to a snow-like pale-blue solid. A tube of liquid oxygen is noticeably attracted by a magnet.


FIG. 45. Burning Sulphur in Oxygen.

Six Specific Physical Properties of Each Gas. — Although every substance has many physical properties, we shall mention only those which are used in chemical work, with occasionally the addition of any peculiar or unexpected quality. It will aid the memory to recall the physical properties of a *gas*, if we note that, as a rule, **only six physical properties** are mentioned: (1) color, (2) taste, (3) odor, (4) density, (5) ease of liquefaction, defined by the critical temperature, (6) solubility, usually in water only.

Specific Chemical Properties of Oxygen. — The chemical properties of pure oxygen are in general like those of atmospheric air, of which it is the active component (p. 13), only more pronounced.

Reactions with Non-metallic Elements. **Sulphur,** when raised in advance to the temperature necessary to start the action, unites vigorously with oxygen (Fig. 45), giving out much heat and producing a familiar gas having

* Each gas has an individual critical temperature (p. 124) above which no pressure, however great, will produce liquefaction. The farther the temperature of a specimen of the gas is below the critical point, the less will be the pressure required to liquefy it.

a pungent odor (sulphur dioxide SO_2). **Phosphorus,** when set on fire, blazes in oxygen very vigorously, forming a white, powdery, solid oxide — phosphorus pentoxide P_2O_5. Burning **carbon,** in the form of charcoal or hard coal, glows brilliantly and is soon burnt up. It leaves an invisible, odorless gas — carbon dioxide CO_2. A stream of **hydrogen** burns with a very hot flame in oxygen, producing *steam,* which condenses on the cooler walls of the containing vessel as droplets of liquid *water.* At high temperatures, oxygen combines readily with one or two other non-metals (*e.g.,* silicon, boron, and arsenic), and to a small extent (1 per cent at 2000°) with nitrogen. It will not combine directly with fluorine, chlorine, bromine, or iodine, although oxides of all these elements can be obtained by using other methods of preparation.

$$S + O_2 \rightarrow SO_2.$$
$$4P + 5O_2 \rightarrow 2P_2O_5.$$
$$C + O_2 \rightarrow CO_2.$$
$$2H_2 + O_2 \rightarrow 2H_2O.$$

Reactions with Metallic Elements. **Iron,** as we have seen (p. 13), rusts exceedingly slowly in air and, even when red-hot, gives hammer-scale, the black solid which is broken off on the anvil, rather deliberately. In pure oxygen, however, iron in the form of picture-wire, if once ignited, will burn with surprising brilliancy, throwing off sparkling globules of the oxide, melted by the heat. This oxide is a black, brittle substance, identical with hammer-scale, and different from rust (ferric oxide Fe_2O_3). It contains, in fact, a smaller proportion of oxygen than does the latter, and is called magnetic oxide of iron Fe_3O_4:

$$3Fe + 2O_2 \rightarrow Fe_3O_4.$$

All the familiar metals, excepting gold, silver, and platinum, when heated, combine with oxygen, some more vigorously, others less vigorously than does iron. Oxides of the three metals just named can also be made, but only by varieties of chemical change other than direct combination.

Reactions with Compounds. **Compound substances,** if they are composed largely or entirely of elements which combine with oxygen, are generally able themselves to interact with oxygen. Usually, they produce a mixture of the same oxides which each element, separately, would give. Hence wood, which is composed of carbon and hydrogen with some oxygen, when burnt in oxygen, produces

carbon dioxide and water vapor. Again, carbon disulphide burns readily, giving carbon dioxide and sulphur dioxide, just as do carbon and sulphur, separately. Ferrous sulphide gives, similarly, sulphur dioxide and magnetic oxide of iron.

The discussion of the formation and properties of **ozone** O_3 (p. 362), which is an oxide of oxygen itself, cannot be taken up until we are in possession of the means of understanding the full significance of the difference in density of the two substances (Chap. XI).

Tests. A Test for Oxygen. — A **test** is a **property which,** because it is easily recognized (a strong color, for example), or because it is especially distinctive, **is commonly employed in recognizing a substance.**

Oxygen, as we have seen (p. 23), *when pure,* is recognized by the fact that a splinter of wood, glowing at one end, bursts into flame when introduced into the gas. Only one other gas (see nitrous oxide) behaves similarly.

Determining Formulæ Again. — To learn the exact nature of interactions like those used as illustrations above, quantitative experiments must of course be made. Thus, for example, a known weight of sulphur, contained in a porcelain boat, is placed in a long combustion tube, fitted up as shown in **Fig. 46.** The U-shaped tube to the right contains a solution of potassium

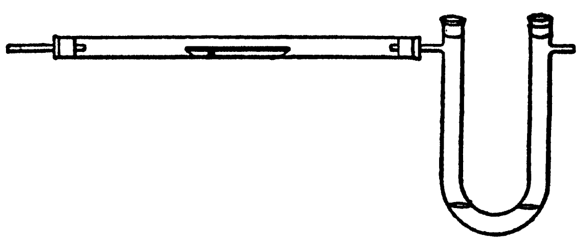


Fig. 46. Measurement of Combining Proportions.

hydroxide, which is capable of absorbing the resulting gas. The oxygen enters from the left. When the combustion tube is heated, the sulphur burns in the oxygen, and the gain in weight of the U-tube shows the weight of the compound produced. By subtracting from this the weight of the sulphur taken, we get the quantity of oxygen with which it has combined and hence we can obtain the percentage composition of the compound.

The proportions of the constituents found by exact experiment and the subsequent steps in the calculation (p. 78) are as follows:

	Percentage		At. Wt.		Factor			÷ 1.561
Sulphur	50.05	=	32.06	×	1.561	=	S × 1.561	S × 1
Oxygen	49.95	=	16.00	×	3.122	=	O × 3.122	O × 2

The formula of the product is therefore SO_2 and the equation (p. 79) is $S + O_2 \rightarrow SO_2$.

Similarly, phosphorus pentoxide may be shown to have the formula P_2O_5, carbon dioxide CO_2, and magnetic oxide of iron Fe_3O_4.

Combustion. — Since oxygen is a component of the atmosphere, chemical actions in which it plays a part are familiar in daily life. Violent union with oxygen is called in popular language **combustion** or burning. Yet since oxygen is only one of many gaseous substances known to the chemist, and similar vigorous interactions with these gases are common, the term has no scientific significance. The union of iron and sulphur, for example, gives out light and heat, and is quite similar in the chemical point of view to combustion.

Oxidation. — The slower union with oxygen which occurs in rusting is called **oxidation.** We shall see later, however, that it has been found convenient to stretch this term so as to cover combinations of other elements than oxygen, and even to include actions not involving combination. At this point we can discuss only oxidation by oxygen.

This process of slow oxidation, although less conspicuous than combustion, is really of greater interest. Thus the **decay of wood** is simply a process of oxidation whereby the same ultimate products (namely, carbon dioxide and water) are formed as by the more rapid, ordinary combustion. Again, large volumes of pure water are mixed with **sewage,** the object being, not simply to dilute the latter, but to introduce water containing oxygen in solution. This has an oxidizing power like that of oxygen gas and, through the agency of bacteria, quickly renders dissolved organic matters innocuous by converting them for the most part into carbon dioxide and water. Thus, a few miles further down the stream, the water may become as suitable for drinking as it was before the sewage entered.

In our own bodies we have likewise a familiar illustration of slow oxidation. Avoiding details, it is sufficient to say that the oxygen, from the air taken into the lungs, combines with the hæmoglobin in the red blood-corpuscles. When blood is placed under the air pump, it effervesces, and oxygen is given off (Mayow, 1669). In this form of loose combination, it is carried by the blood throughout our tissues and there oxidizes the foodstuffs which have been absorbed during digestion. The material products are carbon di-

oxide and water, of which the former is carried back to the lungs by the blood-serum, and finally reaches the air during exhalation. The important product, however, is the heat, given off by the oxidation, which keeps the body warm. If we cease to eat, we become lighter and weaker, showing that a real portion of our structure is gradually being consumed by oxidation.

The opposite of oxidation, the *removal* of oxygen, is spoken of in chemistry as **reduction.** But this term, as we shall see, like oxidation, has been stretched to cover other kinds of chemical change.

Uses of Oxygen. — A number of the practical applications of oxygen have already been mentioned. For example, in the foregoing section we have referred to its use in breathing, its rôle in decay, which is a beneficent process because it removes much useless matter which might otherwise cause disease, and its value in the disposal of sewage. Power and heat for commercial purposes are almost all obtained by the burning of coal, in which oxygen from the air plays a large part. If we had to purchase the oxygen as well as the coal, we should require at least three tons of oxygen for every ton of coal.

Oxygen compressed in cylinders is employed commercially in cutting and welding metals by the oxy-acetylene torch (p. 586), and also in the oxy-hydrogen burner (p. 140). Smaller amounts are used to restore the supply in the atmosphere of submarine boats, and to assist the respiration of pneumonia patients, of aviators, and of mountain-climbers at very great altitudes.

Substances Indifferent to Oxygen. — Finally, since the atmosphere contains so large a proportion of oxygen, substances which do *not* oxidize and, when heated, do *not* burn, have many uses. Gold, silver, and platinum are of this kind (p. 95), and are used for ornaments. The last is used for crucibles in which bodies are heated in the laboratory. Although iron burns in pure oxygen, it does not oxidize in bulk rapidly in the air even when heated, and so is used for making vessels for cooking and in constructing fireproof buildings.

Compounds already fully oxidized are naturally not combustible. Of this nature are sandstone, granite, brick, porcelain, glass, and water. All these are, therefore, fireproof. Moreover, these substances do not give off oxygen when heated. It is this *inactivity* which renders glass and porcelain suitable materials for laboratory apparatus, since they experience no change in weight when heated.

Activity and Stability. — A substance which enters into combination vigorously, as does oxygen, is called chemically **active.** Nitrogen, on the other hand, is relatively **inactive.** An active element, since it combines readily, also holds tenaciously to the matter with which it has combined. An active element implies, therefore, one which is in general difficult to liberate from combination. Its compounds are in general relatively **stable** or **inactive.** Thus, many oxides, and the natural compounds just mentioned (sandstone, granite, brick and porcelain, the last two made from clay), do not lose oxygen even at a white heat and are very *stable.* The compounds of more indifferent elements, on the other hand, are in general relatively easy to decompose. In other words, they are **unstable** or **active.**

The word unstable is frequently misused. Thus, calcium chloride is sometimes said to be unstable, because, when exposed to the air, it takes up moisture and finally dissolves in the water thus acquired. Or phosphorus trichloride is said to be unstable because it interacts with the moisture in the air, or ferrous sulphate is said to be unstable because it is oxidized by the oxygen in the air. Almost every substance, however, will undergo change readily, if a properly selected substance is allowed to come in contact with it. Quicklime, for example, is quickly slaked by water. According to this erroneous view practically every substance is unstable. Quicklime can be distilled, without decomposition, at the temperature of the electric arc, and is extremely stable. Stability refers solely to the effect of energy, usually in the form of heat, upon the substance, while the latter is carefully isolated from all other substances. The interactions of the substance with the components of the air, and with other reagents, must be recorded as separate chemical properties.

Means of Altering the Speed of a Given Chemical Action: By Change of Temperature. — That the same change may proceed with very different speeds according to conditions is a familiar fact. For example, **raising the temperature increases the rapidity of all chemical interactions.** Thus, cold iron combines with oxygen very slowly, giving rust, while white-hot iron sheds quantities of scales of an oxide, formed in the few moments that it is under the blacksmith's hammer. White-hot coal unites with oxygen in the air to form carbon dioxide and seems to disappear before our eyes, while in the cellar, even in warm weather, we observe no appreciable diminution in its amount. Careful measurement, however, shows that, when stored in the open air, coal does lose from 2 to 5 per cent of its heating value. When air is largely excluded, say, by storage under water, there is no loss. No temperature can be found at which the interaction definitely begins. We believe that every such

change proceeds with *some* speed at every temperature. A rough estimation, based on experiment, shows that on an average, other things being equal, **every rise in temperature of ten degrees doubles the amount of material changed per second,** and conversely.

If, on bringing two materials together, the chemist observes no marks of chemical action, he immediately begins cautiously to *heat* the mixture. This appeal to the magnifying effect of a rise in temperature is always made as a matter of course.

The common expressions used in chemistry in describing temperatures, along with the corresponding readings of the thermometer, are as follows:

Incipient red heat,	about	525°.	Yellow heat,	about	1100°.
Dark red heat,	"	700°.	Beginning white heat,	"	1300°.
Bright red heat,	"	950°.	White heat,	"	1500°.

Rapid Self-sustaining Chemical Action and Means of Initiating it. — When a piece of wood is set on fire at one end, the heat produced by the action itself raises the temperature of neighboring portions until their speed of union becomes equal to that of the part originally lighted. In this way the whole becomes finally inflamed. When we blow the blaze out, the great excess of cold air suddenly lowers the temperature of the wood, and of the gas rising from it, and rapid union ceases. Cold water, naturally, lowers the temperature even more promptly. Whether a given set of materials can maintain itself at a temperature proper to violent interaction will depend on the amount of heat developed by the action itself, on the one hand, and the losses of heat by conduction and radiation on the other. If the latter are great, the former must be greater. Thus the union of iron and oxygen *per se* gives heat enough to warm the materials to the burning temperature and leaves much over for radiation. But iron in air, which is four-fifths nitrogen, can receive the oxygen only one-fifth as fast at the start, and even more slowly as, later, the nitrogen accumulates round it. And besides, all the nitrogen has to be heated to, perhaps, 2000°. The task is too great. The union is impeded and the iron is not oxidized fast enough to generate the heat required to maintain everything at this high temperature. Poor conductors of heat, like wood and candles, fare better. Powdered iron, with its particles presenting large surface to the air relatively to the weight of material in each particle to be heated, burns well.

The initial supply of heat required to *start* violent self-supporting chemical actions, of which alone we are here speaking, must not be confused with the heat subsequently developed as the action

proceeds. The latter is usually very much greater (see pp. 260–4). Indeed, the *preliminary supply* varies with circumstances, and may be made as small as we choose by limiting the area first heated and using ordinary precautions against radiation and convection. In practice, a single spark from an induction coil often takes the place of more clumsy methods of raising the temperature. The heat *produced by the interaction itself*, however, is fixed in amount, and depends only on the materials and their quantity.

Heating is not the only means used to give the initial acceleration to a self-sustaining chemical change. The materials in a match-head are capable of undergoing a great transformation. Yet, so slowly does this proceed at ordinary temperatures, that matches may be kept in efficient condition for years. Here a rather violent vibration is employed to hasten the torpid action in a small part of the material, and the heat produced by the resulting action quickly ignites the whole.

The misleading term, **kindling temperature,** is often used in this connection. It gives the impression that there is a definite temperature at which combustion will start. But the temperature is only *one* of the conditions which produce combustion. Finely powdered iron will start burning at a lower temperature than will an iron wire, *because it presents relatively more surface to the gas.* Finely divided lead, known as "lead pyrophorus," catches fire at room temperature. Again, if the oxygen is at less than one atmosphere pressure, the wire will require to reach a higher temperature before combustion will begin. Finally, the vapor of methyl alcohol and air requires to be raised above a red heat before combustion starts, but a pocket cigar-lighter sets fire to this very mixture by means of a *contact agent* (a thin platinum wire) without any other means of heating being required. So that, the conditions under which combustion begins involve the physical condition of the solid, the pressure of the gas or vapor, the presence or absence of a contact agent and the nature of the contact agent, as well as the temperature. No definite kindling temperature can be given, unless the other conditions are specified also. **Kindling conditions** involve several variables, of which the temperature is only one.

Spontaneous Combustion. — Sometimes a mere slow oxidation develops into a combustion, which is then known as **spontaneous combustion.** To understand this, we must note the fact that a given weight of material, say, iron, in combining with oxygen to form a given oxide, will liberate the same total amount of heat whether the union proceeds rapidly or slowly. If the action proceeds slowly, and the material being oxidized is freely exposed to the air, the latter will become heated and will carry off the heat as fast as it is produced. Thus, no particular rise in temperature will occur. If, however, the material is a poor conductor of heat,

like hay or rags, and there is sufficient air for oxidation, but not enough to carry off the heat, the heat may accumulate and a temperature sufficient to start combustion may be reached. Such a situation sometimes arises in haystacks. It occurs also when rags, saturated with oils used in making paints (linseed oil and turpentine), are left in a heap. These oils, in "drying," combine with oxygen from the air and turn into a tough, resinous material. The rags, being poor conductors of heat, finally become hot enough to burst into flame, and serious conflagrations often owe their origin to causes such as this. Oily rags should always be disposed of by burning, or should at least be placed in a closed can of metal. Fires in coal bunkers of ships arise from the same cause, slow oxidation (p. 99), with accumulation of the resulting heat.

Other Means of Altering the Speed of a Given Chemical Change: By Change in Concentration; by Catalysis; by Solution. — Even when the temperature remains constant, there are other changes in the conditions (p. 38) which may be used for accelerating or for moderating the speed of chemical interactions. The most important of these, considered in detail in a later chapter (pp. 269–74), is a change in the **concentration** of the interacting substances. Another is the presence of a **catalytic** or **contact agent.** The condition of **solution** (p. 197) might be accounted still another.

The abatement in the activity of the oxygen found in the air (p. 100), by the nitrogen which is mixed with it, is a question of **concentration.** If the concentration of pure oxygen under atmospheric pressure is taken as unity, that of oxygen in air is only about 0.2. And the speed of interaction of a body, other things being equal, is directly proportional to its concentration. This is not an obscure law, but merely common sense put into definite language. The *opportunity* which one substance has for getting at every part of another will be one factor in determining the speed with which the resulting transformation will take place. And this opportunity, other things being equal, depends on the thickness or density with which the substance is scattered in the region of action. In the case of a gas, this factor is measured by its partial pressure. Hence, lights burn badly at great elevations, where the oxygen is very tenuous. On the other hand, powdered charcoal, which burns feebly in common air, interacts so rapidly when ignited in liquid air, where the oxygen is highly condensed, that an explosion takes place. Again, when oxygen is compressed in contact with barium oxide at 700° it combines to form the peroxide

(p. 90); when the pressure of the oxygen in contact with the latter is reduced, oxygen is liberated (see Chemical equilibrium).

When, without any change in temperature, an extra substance alters the speed of a chemical change, seemingly by its mere presence, without itself suffering any permanent change, we call the foreign body a **catalyst** or contact agent, and the process **catalysis.** The effect of manganese dioxide on the decomposition of potassium chlorate (p. 91) is of this nature. When some of the chlorate is placed in a flask, provided with a two-hole stopper and exit tube, and is melted carefully so as to avoid superheating, scarcely any evolution of oxygen can be perceived at this temperature (368°). If now a pinch of pulverized manganese dioxide, hitherto held in the closed tube, be dropped into the molten mass by turning the end of the tube into a vertical position (Fig. 47), the oxygen is given off in torrents in consequence of the enormous acceleration of the decomposition.* Yet the manganese dioxide (which does not lose oxygen until heated to a much higher temperature, see p. 89) may be recovered unchanged from the residue. Commercial *oxone* (p. 93) always contains a catalyst, a trace of cuprous hydroxide, which hastens the action on water.

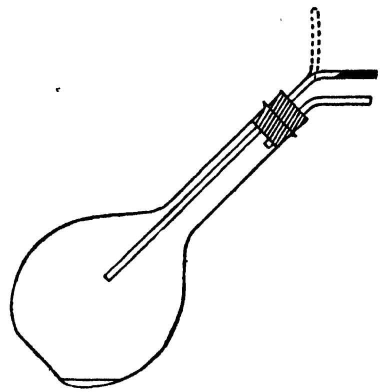


Fig. 47. Catalytic Action of Manganese Dioxide on the Decomposition of Potassium Chlorate.

Catalysts are very frequently used in chemistry. Their presence often enables very complex chemical actions to proceed rapidly at rather low temperatures. Many substances of this class are secreted by animals and plants and play an important part in digestion, fermentation, and other physiological changes.

The removal of organic matter from sewage (p. 97) is, in part at least, a process of **decay.** Decay is, essentially, slow oxidation promoted by bacteria and other organisms. It takes place also in animal or vegetable matter on land. It proceeds, however, as a rule, only when the material is moist, and water may consequently be considered as a catalyst for the process. Dried fruits, dried leaves, and dried meat, whether dried by the sun or artificially, decay very slowly. Hence desiccated foods are now manufactured in large quantity, since besides their permanence they possess the advantages of

* To avoid injury from an explosion, it is advisable to wrap the flask in a towel, before turning the tube.

much smaller weight and bulk in shipping. When they are transferred to a moist atmosphere, bacteria and moulds begin to grow and multiply in them, and decay sets in.

It is found that many other actions owe what appears to be their normal speed to the presence of a trace of water vapor. Thus many of the elements show no visible tendency to unite with carefully dried oxygen, even when they are strongly heated in it. Addition of a trace of moisture, however, brings about instant combustion. So water is to be regarded as one of the commonest contact agents.

Catalysis is a topic of extreme interest, from both the theoretical and the practical points of view. The ability of manganese dioxide to hasten the decomposition of potassium chlorate, although remaining itself unchanged at the end of the reaction, is only the first of many cases of catalysis which will come up for discussion in this volume. Many of our most important industrial processes are catalytic (pp. 419, 422, 507, 531). It used to be the custom of chemists to make a mystery of catalysis, and to regard it as something beyond our powers of investigation. Now we believe that catalysts actually take a direct part in the chemical reactions that they accelerate, forming unstable intermediate compounds and being regenerated as these are decomposed. The chamber process for the manufacture of sulphuric acid (pp. 422–3) is a good instance. In the very case of potassium chlorate and manganese dioxide here under discussion, it may be noted that if, initially, a crystalline form of the dioxide is employed, the final product is in the form of a fine powder. Although the catalyst does not alter in chemical composition, its physical state is frequently quite changed by its passage through the cycle of reactions that occurs (see p. 531).

Many cases of retardation of an action by a catalytic agent are known. Thus a little benzyl alcohol or mannite added to the solution will retard the oxidation of sulphites by the air (Bigelow). Acetanilide is used commercially to retard the decomposition of hydrogen peroxide in aqueous solution. Hence positive and negative catalysis both occur.

The effect of **solution** in hastening a chemical change was seen when we examined the interaction of sodium chloride and silver nitrate (p. 31). With the solutions the action was seemingly instantaneous. If we had attempted to bring it about by rubbing the dry substances in a mortar, hours of work would have left much of the original bodies still unchanged. Even heating would not have produced so prompt an effect. It is obvious that the intimate access which every part of each solution gains to every part of the other accounts to some extent for the difference (see Ionization). Chemical actions, as will be seen in the sequel, are very frequently carried out in aqueous solution in order to take advantage of the favorable influence of this condition.

Exercises. — 1. Enumerate, with examples, the methods of nomenclature employed by chemists to distinguish different degrees of oxidation of the same element.

2. Define and illustrate: density of a gas (p. 93), density of a solid or liquid (p. 9).

3. Enumerate the classes of facts given under the heads of (*a*) Physical, and (*b*) Chemical Properties of oxygen, respectively.

4. What weight of oxygen may be obtained by heating 30 g. of barium peroxide (p. 90)? In solving this problem, pay minute attention to the rules (pp. 82–3).

5. What weight of potassium chlorate would you require to heat in order to obtain the same weight of oxygen as in Exercise 4?

6. How should you show that, in the making of oxygen from a mixture of potassium chlorate and manganese dioxide, the latter remains unchanged? Which properties (p. 104) are you employing for this purpose?

7. The substances, like phosphorus and sulphur, which burn rapidly in ordinary oxygen, combine very, very slowly (even when heated) with oxygen which has been freed from moisture by careful drying. How is this effect of water to be classified?

8. Discuss the union of iron and sulphur (p. 22) and the decomposition of mercuric oxide (p. 23) in their relation to the explanations on pp. 100–2.

9. When iron wire burns in oxygen, the oxide of iron falls in melted globules, and no smoke is produced, while when phosphorus is burned, all the oxide goes off as smoke, and nothing remains in the spoon. Explain this difference.

10. What percentage by weight of free oxygen is obtained by heating: (*a*) mercuric oxide, (*b*) potassium nitrate, (*c*) potassium chlorate? At $1.50, $0.15, and $0.20 per kilogram, respectively, which is the cheapest source of oxygen?

11. Why does a forced draft make a fire burn more rapidly?

12. Why does a naked flame sometimes cause an explosion in a mine, when the air of the mine is filled with coal dust?

13. What is the percentage by weight of oxygen in (*a*) barium monoxide, (*b*) barium peroxide, (*c*) sodium peroxide?

14. What is the percentage by weight of iron in (*a*) ferric oxide (p. 17), (*b*) magnetic oxide of iron (p. 95)?

15. How many grams of oxygen would you obtain by adding excess water to 100 g. of sodium peroxide (p. 93)?

16. What weight of potassium nitrate (p. 89) would you need to take to obtain 10 g. of oxygen?

17. What would be the volume of 32 g. of oxygen at 0° and 760 mm. barometric pressure (p. 93)? What would be the weight of the corresponding volume of (*a*) hydrogen, (*b*) air, under the same conditions?

18. 10 c.c. of liquid oxygen at −182.5° (p. 94) are allowed to evaporate. What is the volume of the resulting gas at 0° and 760 mm.?

19. Define combustion; kindling conditions; oxidation; reduction; spontaneous combustion.

20. Define activity; stability. Illustrate by examples from Chapters I–VI.

READING REFERENCES

Kendall; At Home among the Atoms, Chapter VII.

Alembic Club Reprints, Nos. 7 and 8. The Discovery of Oxygen (Priestley and Scheele).

CHAPTER VII

THE MEASUREMENT OF QUANTITY IN GASES. THE KINETIC-MOLECULAR HYPOTHESIS

We have spoken of measuring the proportion by weight of the oxygen used in several chemical changes, but in our illustrations we have never weighed the gas itself. We have always (*e.g.*, p. 96) obtained its quantity by subtracting the weights of solid or liquid bodies. In practice this method often serves the purpose.

Our preference for weighing as a means of ascertaining quantity of matter is largely due to the fact that the weight is independent of the physical or even chemical condition of the substance. Yet, with proper precautions, we may learn the quantity of matter by means of any other attributes which are proportional to it. Now the volume is such an attribute. In determining the quantity of a liquid, where rapidity with no extreme accuracy is desired, the volume is frequently measured. In the case of gases the error made in measuring the volume is less, as a rule, than in measuring the weight.

The Variable Concentration of Gases. — A little experience with gases soon shows us that measurement of volume alone does not necessarily give any definite idea of the quantity of matter present. The denseness with which the gaseous matter is packed (the **concentration** of the gas) in the vessel must somehow be defined, as well as its volume, in order that there may be specification of the quantity of matter.

Gases vary markedly in chemical activity with changes in their concentration (compare p. 102), and thus the consideration of this condition (p. 38) is continually forced upon the chemist. Solids and liquids do not alter their denseness of packing (concentration) very noticeably even when compressed severely or changed in temperature. So that concentration need not be considered in the case of pure bodies in the solid or liquid forms. Such substances can be scattered through a variable space by solution in some solvent, however, and

then their degree of packing or concentration becomes an important factor in *their* chemical behavior also.

The principle used for estimating the concentration of a gas may be illustrated by means of the arrangement in Fig. 48. Except that a little gas (any gas will do) remains shut off by the mercury in the left limb of the tube, the whole apparatus has been evacuated. The reservoir can be turned upward, and thus larger amounts of mercury may be introduced into the tube.

Now the portion of the mercury below the dotted line is essentially a balance, that is to say, it will move in one direction or the other if the stresses on either side change. At present these stresses must be equal. On the right pan of the balance, so to speak, the stress is represented by the pressure exerted by the column of mercury above the dotted line. As there is nothing in the tube above this mercury, this pressure is all that this side of the balance sustains. On the left pan of the balance there must be an equal stress, and this stress can be caused only by the gas confined in the shorter limb. The nature of a gas suggests that this stress must be exercised on the walls of the tube also, although they, of course, do not normally exhibit its effects. This stress we call the **pressure** of the gas.

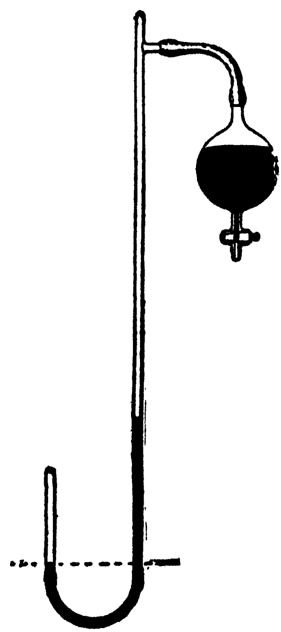


FIG. 48. Effect of Pressure on Concentration of a Gas.

The height of the surface of the mercury on the right above that on the left having been measured, more mercury may now be added from the reservoir, and the difference in the two levels again noted. The gas cannot have diminished in amount, yet it now occupies a smaller space, and is, therefore, packed more closely — its concentration is greater than before. If, for example, the difference in level is now twice as great, it will be found that the concentration of the gas is also twice as great (its volume having become half of the original volume). Whatever amount of mercury is added, we shall always find that the concentration of the gas is proportional to the excess height of mercury, and hence proportional to the pressure exerted thereby. The pres-

sure of mercury on one side must, however, be equal to the stress or pressure or tension of the gas on the other side which balances it. Hence, **the concentrations of a sample of any gas are proportional to the corresponding pressures it exercises.** We determine, therefore, the denseness with which any sample of gas is packed by measuring its pressure.

Method of Allowing for Varying Concentration in Measuring Quantity in Gases. — The principle just stated is applied to the measurement of the quantity of matter in a sample of gas by permitting the concentration of the sample to alter until it is equal to that of the atmosphere at the moment. Then we read off the volume now occupied, and simultaneously we ascertain the pressure by observing that of the atmosphere. Each of these two operations is facilitated by a special arrangement of apparatus.

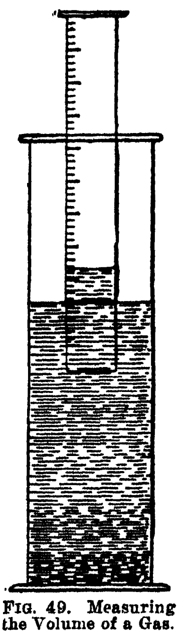


Fig. 49. Measuring the Volume of a Gas.

A gas to be measured is always confined so that some liquid constitutes one part of the barrier to its escape. The very simplest form of the apparatus is shown in Fig. 49. To render the concentration (and pressure) of the gas in this case equal to that of the atmosphere, the cylinder containing the gas is lowered until the levels of the liquid inside and outside are the same. When the system is in this condition the stress of the gas on the inner surface must be equal to that of the atmosphere on the outer one, otherwise movement of the liquid would occur. The volume of the gas is then read directly from the graduation on the cylinder. When special modes of admitting or handling the gas have to be provided for, the apparatus may be more complex. But the principle of adjustment is always the same. In exact work, mercury is employed to confine the gas. Water serves the purpose of rough work with gases which, like oxygen, are but slightly soluble in it. When water is used, the volume is too great by the space occupied by the vapor of the water which is mixed with the gas (see Mixed gases, p. 116), and a correction must always be made on this account.

The pressure or tension of the atmosphere at any moment is measured by means of a **barometer** — a modification of the apparatus in Fig. 48.

A simple form of barometer is shown in Fig. 50 (tube on right of diagram only). A glass tube, about 1 meter long and closed at one end, is completely filled with mercury and carefully inverted, with its open end dipping into a mercury reservoir. The mercury falls inside the tube, leaving a vacuum at the top, until the pressure of the mercury column inside balances the pressure of the air outside. The atmospheric pressure is therefore expressed by the barometer as equivalent to the pressure exerted by so many *millimeters of mercury*. For accurate work, all readings obtained must be reduced to a standard temperature (0° C.), by correcting for the expansion of mercury above that temperature.

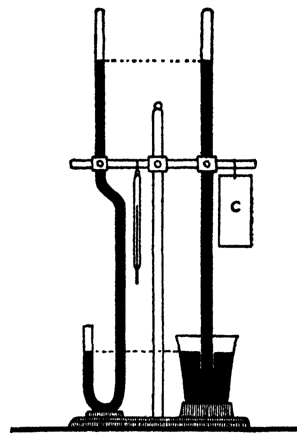


FIG. 50. Barometer (two forms).

A more practical form of barometer for laboratory use consists of a bent tube containing mercury (Fig. 50, left half of diagram). The short limb (to the left) is open and the pressure of the atmosphere is exercised on the surface of the mercury there. The longer limb (to the right) is closed at the top and in it there is no gas above the mercury. Hence, reading the difference in the heights at which the mercury stands in the two limbs gives us a measure of the pressure of the atmosphere and of any specimen of gas which is at the same pressure.

Boyle's Law. — The recorded results of measurements made as above at different times, or at different places, when the atmospheric pressures are different, are still unsatisfactory because the data for samples of the same kind of gas differ in the value of the pressure as well as in that of the volume. To make the results easily comparable in respect to the amount of matter they represent, one further step is needed. All the data are recalculated so as to show the volume each sample would have occupied if the pressure had been equal to that exerted by 760 mm. of mercury, which is the average height of the barometer at the sea level in 45° of latitude.

We have seen that the concentration of a given quantity of a gas is proportional to its pressure (p. 108). But, volume occupied is the inverse of concentration. Thus, the same rule may be stated in the form: **The volume occupied by the same sample of any gas at constant temperature is inversely proportional to the pressure.** The

fact was discovered by Boyle (1660), who stated it in this way. In still other words, the product of the pressure (P) and the volume (V) of a given sample of gas at a fixed temperature is a constant; $PV = K$.

A numerical illustration will show the mode of applying this rule. We measure 200 c.c. of a gas at atmospheric pressure, and the barometer reads 742 mm. The question is: What would be the volume of this amount of gas at 760 mm. barometric pressure? It will be $200 \times \frac{742}{760}$ c.c. = volume at 760 mm. It is unnecessary to use any formula, but absolutely essential to ask: Is the new pressure greater or less than the old? Here it is *greater*. Hence, according to the law, the new volume will be *less*, so that the fraction must be arranged with the smaller number in the numerator.

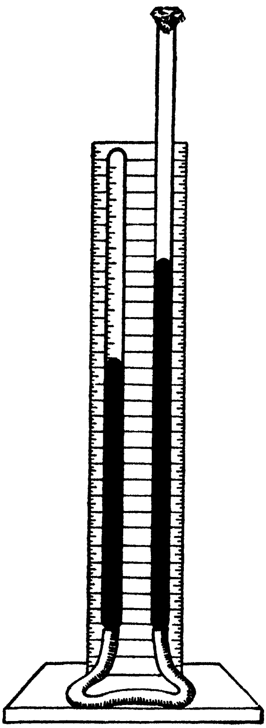


FIG. 51. Apparatus to Illustrate Boyle's Law.

Boyle's law may be illustrated in the lecture-room by using the apparatus shown in Fig. 51. A volume of air is enclosed over mercury in a glass tube, and the pressure under which it exists can be varied by moving the side tube up or down. Scales on the two tubes enable us to read volumes and pressures accurately.

The mercury levels on the two sides are first made equal, and the barometric height noted. The gas now occupies a certain volume (say 20.1 c.c.) under the current atmospheric pressure (say 750 mm.). The side tube is now raised, and the difference in the mercury levels on the two sides is read off from the scales. This is the *extra* pressure we have put upon the gas; it is that exerted by (say) 250 mm. of mercury. The *total* pressure upon the gas inside the tube is therefore $750 + 250 = 1000$ mm. The volume is now noted, and found to be 15.0 c.c.

How does this observed volume check up with Boyle's law? We increased the pressure in the ratio 1000 : 750. We ought therefore to *decrease* the volume, and the new volume should be 750/1000 times the original one. Our calculated value is therefore $20.1 \times 750/1000 = 15.1$ c.c. Allowing for probable errors in reading the mercury levels, this is in agreement with the observed value.

It is good practice to work out a few numerical examples in this way, and to compare your results with what you actually observe. Include *reduced* pressures as well as *increased* ones.

The curve *AB* in Fig. 52 shows Boyle's law in graphical form. Pressures *P* are plotted vertically and volumes *V* horizontally. At any fixed temperature, *V* is inversely proportional to *P*, or $P = K/V$, where *K* is a constant. If then we take a volume V_1 of gas under a pressure P_1, and change the pressure to P_2, the new volume

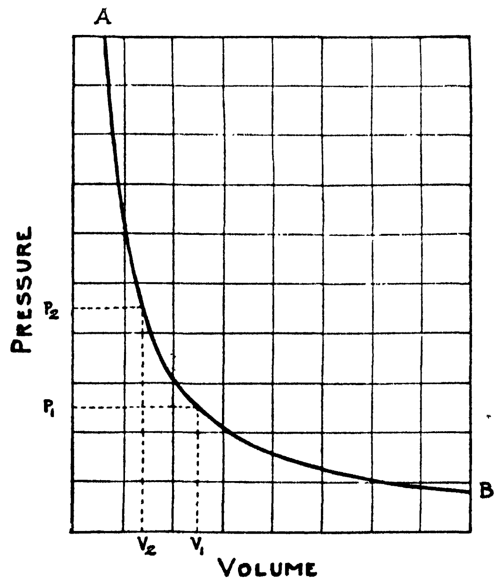


FIG. 52. Graphical Representation of Boyle's Law.

V_2 is readily calculated. For $P_1 = K/V_1$, and $P_2 = K/V_2$. Dividing one equation by the other, we obtain: $P_1/P_2 = V_2/V_1$; or $P_1V_1 = P_2V_2$; or $V_2 = P_1V_1/P_2$. Similarly, if we are given P_1, V_1, and V_2, then $P_2 = P_1V_1/V_2$. Test this out upon the two values of *P* and *V* indicated on the graph.

Boyle's law states the facts with sufficient accuracy for all ordinary purposes. But in reality no two gases behave *precisely* alike in respect to change in concentration when the pressure is altered (see p. 123). The same gas does not even behave in precisely the same way at high, intermediate, and low pressures. The ideal gas, which should behave uniformly, we call the *perfect* gas. With most gases, at low pressures concentration increases a little more, and at very high pressures much less than the rule indicates (see p. 124).

Relation of Volume to Temperature (Charles' Law).—In the foregoing we have assumed that there were no temperature effects. But, as a matter of fact, a rise in temperature will at once produce an increase, and a fall in temperature a decrease in the pressure of an enclosed sample of a gas. Hence a record of the pressure alone will fail to indicate the concentration definitely, and volume and pressure together will still leave the amount of material unspecified. The temperature must, therefore, be given as well.

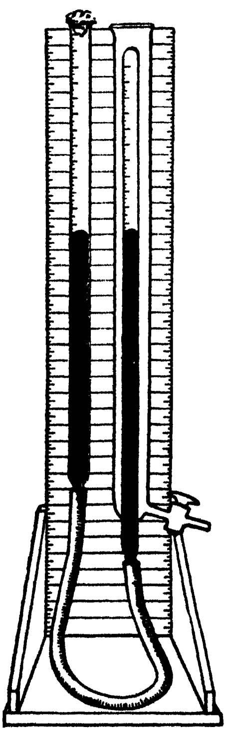


FIG. 53. Apparatus to Illustrate Charles' Law.

Our descriptions of different samples of gas, at different temperatures, having thus become once more incomparable, we apply the same kind of remedy as before. We calculate the volume which each specimen of gas would occupy at 0° C.

The rule for this calculation may be demonstrated in a rough way in the lecture room by means of the apparatus shown in Fig. 53. It is similar to that already described on p. 110, but the exterior tube on the right enables us to vary the temperature of our enclosed gas. The most convenient temperature range to study is between 0° and 100° C. The former is reached by packing the space between the tubes with a mush of ice and water, the latter by blowing a rapid current of steam through the large tube.

About one-half of the closed inner tube on the right is occupied by the gas. The mercury levels are made alike at the beginning of the experiment, and the pressure of the gas is maintained constantly the same as that of the atmosphere by adjusting the tube on the left. When, now, the volume occupied by the gas at 0° is read, and warmer water is introduced, we find that the volume gains $\frac{1}{273}$ of its value at 0° for every degree through which its temperature rises. If it is cooled below 0°, it loses $\frac{1}{273}$ of its volume at 0° for every degree through which the temperature is lowered. Observation gives practically the same value for all gases.

If we, for convenience, take a volume of 273 c.c. of a gas at 0° and warm this through 1°, then at 1° its volume, having gained $\frac{1}{273}$

of its original value, becomes 274 c.c. At 2° it has gained another $\frac{1}{273}$ of the volume it had at 0° and becomes therefore 275 c.c., etc. If cooled below 0° it loses $\frac{1}{273}$ of the volume, becoming 272 c.c., etc.

If the gas be heated to 100° it gains $\frac{100}{273}$ of its volume at 0° and becomes 373 c.c. We might infer that if it were cooled through 273° from 0° it would lose $\frac{273}{273}$ of its volume, in other words, it would

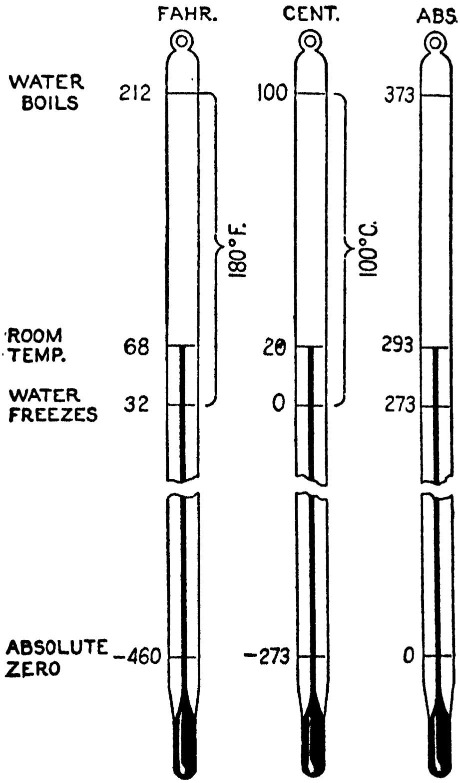


FIG. 54. Temperature Scales Compared.

disappear. This temperature (the **absolute zero**) has not yet been reached, and in any case all gases would liquefy before reaching it. Our statements apply to ordinary temperatures only, and within them the law holds with considerable strictness.

By applying an arithmetical device, we can state the rule contained in the above statements in a form which makes its use in calculations quite easy. The device consists in *adding 273 alge-*

braically to all temperatures on the Centigrade scale. The temperature, when 273 has been added, is called the **absolute temperature** (see Fig. 54). Our second general rule then reads as follows: **The volumes assumed by a sample of gas at different temperatures, the pressure remaining constant, are directly proportional to the corresponding absolute temperatures.** This is the modern way of stating a fact which was first discovered by Charles of Paris (1787).

The discovery of this fact is frequently attributed to Dalton, who first published an investigation of the subject, embodying this result, in 1801, or to Gay-Lussac, who made a more complete investigation in 1802. Inasmuch, however, as in chemistry we have another important principle known as Gay-Lussac's law, and several connected with the name of Dalton, it is on the whole fortunate that we are justified in attributing this discovery to Charles.

The application of this law may best be illustrated by an example. We obtain 200 c.c of a gas at 17° and wish to know what volume it would occupy at 0°. To answer the question, we convert the Centigrade temperatures to the absolute scale by adding, algebraically, 273 to each. Thus $200 \times \frac{273}{290}$ = the volume at 0° required. No formula is needed. We simply ask whether the new temperature is higher or lower than the old one. Here it is *lower*. The new volume will therefore be *smaller* than the old one. So we take care to place the smaller number in the numerator.

The law may be put in mathematical form (see below). It is preferable, however, that beginners should use the method employed in the illustration given in the preceding paragraph. Simple mathematical expressions, like the one representing this law, are not made to save us the trouble of remembering the law itself, and it would be unfortunate if their use led us to forget it.

A lecture demonstration of Charles' law may be given with the help of the apparatus already described (Fig. 53).

We first adjust our mercury levels until they are equal, and note the volume occupied by our sample (say 30.2 c.c.) at the temperature of the room (say 20° C.). Suppose we next raise the temperature to 100° by means of steam. We wait until the gas has reached the new temperature, and bring the pressure back to the original value by lowering the side tube until the mercury levels are again equal. Finally the new volume is read off on the scale; it is observed to be 38.5 c.c.

Let us compare this with the value calculated from Charles' law. We have increased our temperature from $273 + 20 = 293°$ Absolute to $273 + 100 = 373°$ Abs.; our volume should be increased, therefore, in the proportion 373/293. This would make our final volume $30.2 \times 373/293 = 38.4$ c.c. Again the agreement is within experimental errors.

Charles' law is shown graphically by the line *OA* in Fig. 55. Pressures *P* are plotted vertically and absolute temperatures *T*

horizontally. At any fixed pressure, V is directly proportional to T, or $V = K'T$, where K' is a constant. If therefore we take a volume V_1 of gas at a temperature T_1 and change its temperature to T_2, the new volume V_2 is V_1V_2/T_1. (Confirm this for yourself by proceeding as we did for Boyle's law on p. 111). Similarly, if we know V_1, T_1, and V_2, then $T_2 = V_2T_1/V_1$. Note that it is possible to solve any problem on Charles' law immediately from the graph by drawing a line through the point representing our original conditions (say the point B) and the origin. If we now change from T_1 to T_2,

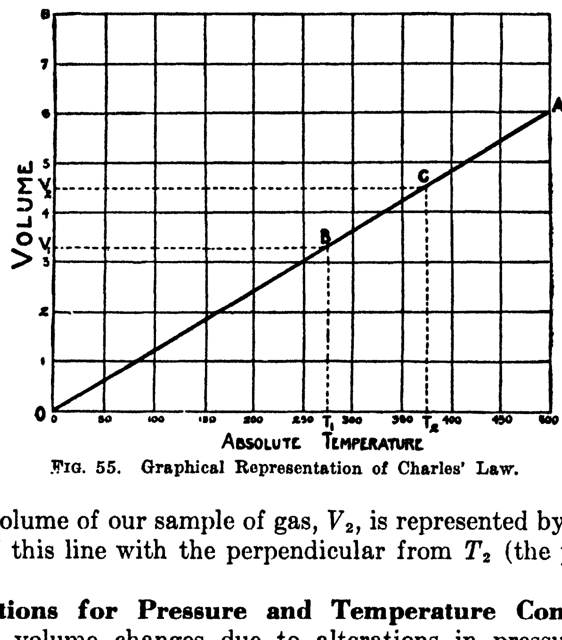


FIG. 55. Graphical Representation of Charles' Law.

the new volume of our sample of gas, V_2, is represented by the intersection of this line with the perpendicular from T_2 (the point C).

Corrections for Pressure and Temperature Combined. — Since the volume changes due to alterations in pressure and in temperature are independent of one another, the corrections may be made either separately or together. The latter is more convenient. Thus, a sample of gas occupies 200 c.c. at 17° and 742 mm., what will be the volume under **standard conditions,** namely **0° and 760 mm. pressure?**

$$\text{New volume} = 200 \times \frac{273}{290} \times \frac{742}{760} = 183.8 \text{ c.c.}$$

If a sample of a gas is heated and its *volume is kept constant,* then we find that its *pressure is directly proportional to the abso-*

lute temperature. This is not a third law distinct from that of Boyle and of Charles, but is derived by combining the two.

Mixed Gases (Dalton's Law). — Different gases at the same temperature, provided they do not interact chemically, exert no influence at all upon each other when mixed. Each component of the mixture behaves as if all the others were absent and it alone were in occupation of the whole available volume. Thus if we mix 100 c.c. of oxygen and 400 c.c. of nitrogen, each at one atmosphere pressure, the resultant gas occupies 500 c.c. at this same pressure, but the oxygen acts as if it were under a pressure of only *one-fifth of an atmosphere*, while the nitrogen acts as if it were under a pressure of only *four-fifths of an atmosphere.* This may be generalized into the **law of partial pressures,** first formulated by Dalton in 1807: **The pressure exercised by each component in a gaseous mixture is proportional to its concentration in the mixture, and the total pressure of the gas is equal to the sum of those of its components.**

This law is particularly useful in correcting to standard conditions a given volume of a gas which has been collected over water, since such a specimen necessarily contains water vapor. The partial pressure of this, called **aqueous tension** (p. 166), which is definite for each temperature, must be subtracted from the total pressure in order to obtain the partial pressure of the gas being measured, and the remainder must be used as the pressure of this gas in any calculation. Thus, in a gas measured over water at 22°, the total pressure includes 19.7 mm. pressure of water vapor (the aqueous tension at 22°, see Appendix IV). Hence 150 c.c. of gas over water at 22° and 750 mm. is the same in amount as 150 c.c. of the same gas in dry condition at 22° and 730.3 mm. (there being simply 150 c.c. of water vapor at 19.7 mm. mixed with it). To obtain the volume of dry gas at 0° and 760 mm. we have the expression

$$150 \times \frac{273}{295} \times \frac{730.3}{760}.$$

Densities of Gases. — The application of the laws of Boyle and Charles enables us to express the quantities of matter in samples of gases in a definite and readily comparable manner. In describing chemical changes, however, it is continually necessary to express quantities of gases by weight. The relation between volume and weight for each kind of gas must, therefore, be ascertained. If we know, for example, the weight of one liter of each gas at 0° and 760 mm. pressure, conversion to other weights, volumes, temperatures, and pressures can be made. The one-thousandth part of this value,

the weight of 1 c.c., is the true **density** of the **gas.** Often, however, the relative weights of equal volumes, with that of air or hydrogen as unity, receive this name (compare p. 93).

For most chemical purposes a high degree of accuracy is not required. The most direct method is to employ a light flask of 125-150 c.c. capacity, provided with a rubber stopper and stopcock (Fig. 56). By means of an air-pump the contents of the flask are removed, and it is weighed. This gives the weight of the empty vessel. The gas, whose density is to be ascertained, is then admitted, and care is taken that it finally fills the flask at the pressure of the atmosphere. The flask is closed and weighed again. The increase represents the weight of the gas. At the same time the temperature and barometric pressure are read. The volume is determined by displacing the gas once more from the flask, filling with water, and weighing again. The difference in weight between the empty flask and the flask full of water, in grams, enables us to calculate the volume of the content of the flask in cubic centimeters. This volume is reduced to 0° and 760 mm. by the rules discussed above, and we have then a volume of the gas and the corresponding weight.



FIG. 56. Measurement of the Density of a Gas.

To illustrate, let us suppose that the volume of the flask is 200 c.c. and that it is filled with oxygen at 17° and 742 mm. The weight of the gas is found to be 0.26 g. We ascertained (p. 115) by calculation that at 0° and 760 mm. this volume would be 183.8 c.c. The weight of a liter is given by the proportion 183.8 : 0.26 :: 1000 : x. Here $x = 1.415$ g. When the operation is performed carefully, and the weighing carried to the nearest milligram instead of the nearest centigram, a result more nearly approaching the exact one (1.429) may easily be reached.

To get the density of oxygen referred to hydrogen as unity, we must divide the answer by the weight of a liter of hydrogen (0.0899 g.). In the above case the quotient is 15.74. The accepted value is 15.88. The density referred to air as unity is similarly obtained by dividing by 1.293, the weight of a liter of air at 0° and 760 mm. pressure.

The values of the densities of gases are of great significance from the chemical point of view. A number of them are given later in connection with the discussion of molar weights (see p. 185).

Vapor Densities. — The densities of the vapors obtained when liquids and solids are heated are as important to the chemist as those of gases and, solids and liquids being more numerous, are even more frequently measured.

A modification of the flask just described is used. A tempera-

ture sufficiently high to vaporize the substance must be employed. The volume is reduced by rule to 0° and 760 mm., and the density, in this case known as the **vapor density** (wt. of 1 c.c.), is calculated as before. The reduction to 0° and 760 mm. pressure by rule gives, of course, a fictitious result. The vapor would condense to the liquid form before 0° was reached, if the cooling were actually carried out. But the value for the density *as it would be* at 0° and 760 mm. has to be calculated to facilitate comparison with the corresponding values for other substances. The results have no physical significance, but are highly important to the chemist.

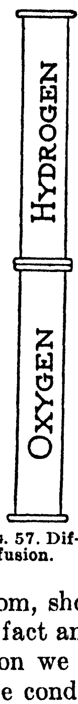


FIG. 57. Diffusion.

Diffusion. — When two cylinders, one filled with hydrogen and one with oxygen, are placed mouth to mouth (Fig. 57), so that the one containing hydrogen is uppermost, since the oxygen in the lower cylinder is nearly 16 times as heavy as the hydrogen (p. 117), we might expect the gases to remain in their respective cylinders. The oxygen, however, makes its way into the hydrogen above it, and the hydrogen penetrates into the oxygen in the lower cylinder so that, in a short time, the gases are perfectly mixed, just as if gravity did not exist. The same phenomenon is observed when, in everyday life, a bottle of scent is opened. The vapor, on escaping, begins to penetrate in all directions through the room, showing its presence by its odor. The material of gases has in fact an independent power of locomotion. The resulting phenomenon we call *diffusion.* It is constant in rate for each gas under like conditions, and hydrogen has the greatest speed of diffusion of all the gases.

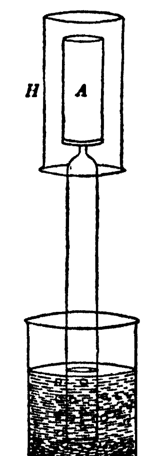


FIG. 58. Apparatus for Comparing Rates of Diffusion.

The phenomena of diffusion must not be confused with cases like the pouring of hydrogen upward to displace air in an inverted jar. In this case the gas flows *en masse,* and the gravity effect is the very one on which we depend for the success of the experiment. It is when hydrogen scatters itself in a somewhat slower way, and downward and sideways as well as upward, that we have diffusion. The word indicates the *scattering* rather than the *flowing* nature of the phenomenon.

The different rates of diffusion of different gases are easily shown by com-

paring their several speeds with that of air, when both pass through a wall of unglazed, porous porcelain.

The porous cylinder *A* (Fig. 58) contains air and is connected by a rubber stopper with a wide tube which dips beneath the surface of the water. When a cylinder *H* containing hydrogen is brought over it, rapid escape of gas takes place through the water, showing that a rise in pressure has taken place inside the porous vessel. Before the cylinder of hydrogen approached the porous vessel, the air was moving both outwards and inwards through the porcelain, but, being the same gas, the speed of motion was equal in both directions, and therefore the pressure inside was not affected. It is important to note that there was at no time rest, there was simply equal motion in both directions. When the hydrogen atmosphere surrounded the cylinder, the hydrogen gas moved more rapidly into the cylinder than the air inside could move out, and hence an excess of pressure quickly arose in the interior of the vessel.

Exact measurement shows that the lighter a gas is in bulk, the faster its parts move by diffusion in any direction. The rate is inversely proportional to the square root of the density of the gas. Thus, for hydrogen and oxygen it is in the ratio $\sqrt{1.429} : \sqrt{0.0899}$, or 4.0 to 1.

The Kinetic-Molecular Hypothesis

Just as we can thoroughly understand the behavior of a watch or an automobile engine only if we know the details of its structure, and how the parts work, so we can understand the physical and chemical behavior of matter in masses only if we are familiar with its ultimate mechanism. Hence we must now take up the study of the structure of matter in the gaseous state.

In order to *explain* the applicability of the laws of Boyle and of Charles to gases in general, a **hypothesis** (p. 34) has been devised by chemists. In the course of time, evidence has been accumulated which verifies this hypothesis beyond all possibility of doubt. The hypothesis is known as the **kinetic-molecular hypothesis,** from the two main postulates upon which it is based.

In the first place, it is assumed that all matter in the gaseous state is composed of exceedingly minute discrete particles or **molecules,** all molecules of any particular substance being normally alike in nature and in mass. In solids and liquids, these particles are fairly closely packed, and the cohesive forces between neighboring particles, for matter in the solid state, may be sufficiently strong to cause the individual molecules to lose their distinct characteristics altogether (see pp. 68–72). In gases, on the contrary, the molecules are widely scattered, with much vacant space between them.

The second postulate is that the molecules of all substances under ordinary conditions are in rapid motion, and consequently

possess **kinetic energy.** In liquids this motion is restricted, by cohesive forces between the particles, within a definite volume; in solids the restrictions are still more rigid (see p. 176). In a gas, however, the molecules are free to distribute themselves throughout the whole of the containing vessel, and by continually striking the walls of this vessel they produce **pressure.**

The Properties of Gases. — A very noticeable fact about gases is that they *can be compressed* to an enormous extent. Oxygen at 760 mm., for example, can be reduced by pressure to one two-hundredth of its volume, or even less. The compression does not significantly affect the individual molecules, and therefore does not diminish the volume actually occupied by the oxygen, but it crowds the molecules closer together and **diminishes** to one two-hundredth **the space** between them. Compressing a gas is essentially, in fact, compressing the *empty space* of which it chiefly consists. To understand what follows, the reader must keep constantly before him a mental image of a jar of gas as consisting of extremely small particles separated by relatively wide, empty spaces. The molecules are in rapid motion and move in straight lines, excepting when they strike one another or the walls of the vessel.

The most remarkable property of a gas, considering the looseness with which its material is packed, is the total *absence* in it *of any tendency to settling.* Since the molecules cannot be at rest upon one another, as the great *compressibility* shows, we are driven to conclude that not only are they **widely separated from one another,** but that they occupy the space, otherwise a complete vacuum, by **constantly moving about in all directions.** But a moving aggregate of particles which does not even finally settle must be in perpetual motion. We must, therefore, believe the molecules to be wholly unlike larger bodies of matter (*e.g.*, a tennis-ball) in having **perfect elasticity,** in consequence of which they undergo no loss of energy after a collision. They must continually strike the walls of the vessel and one another and rebound, yet without loss of motion. The fact that each gas is normally *homogeneous* (exceptional cases will be discussed later, see p. 193) requires the supposition that **all the molecules** of a pure gas are **closely alike.**

The *diffusibility* of gases is due to the **motion of the molecules,** and their *permeability* to the **space** available to receive molecules of another gas. These two modes of behavior involve no additional molecular properties. The word "diffusion" is often thought to mean the property of a given mass of gas in virtue of which an-

other gas can mix with the given mass. This property is not diffusibility but permeability. It is the other gas, which makes its way into the given gas, which is diffusing. Diffusion is spontaneous motion of the parts of a gas *away from* their original location. Unless this motion is into an empty space, the diffusing molecules must, of course, move into another body of gas. In the case of the jars of hydrogen and oxygen (p. 118), each gas moved in part *out of* its original jar (diffused), and each received parts of the other gas *into* its jar (was permeated).

From the diffusion results obtained by experiment with any particular gas, the *average speed* at which the molecules of which it is composed are moving can be calculated. For the hydrogen molecule at room temperature, this speed is 1840 meters per second, or faster than a rifle bullet. The average speed of the oxygen molecule under the same conditions is one-quarter of this value, or 460 meters per second.

Boyle's Law and Charles' Law. — Returning now to *Boyle's law* (p. 109), the thing to be accounted for is that when a sample of a gas diminishes in volume, its pressure increases in the same proportion. Let the diagram (Fig. 59) represent a cylinder with a movable piston, upon which weights may be placed to resist the pressure. Now the pressure exercised by the gas under the piston cannot be like the pressure of the hand upon a table, since we have just assumed that the particles are not even approximately at rest, and the spaces between them are enormous compared with the size of the molecules themselves. The gaseous pressure must therefore be attributed to the colossal hailstorm which their innumerable impacts upon the piston produce. If this is the case, the compressing of a gas must consist simply in moving the partition downwards, so that the particles as they fly about are gradually restricted to a smaller and smaller space. Their paths become on an average shorter and shorter. Their impacts upon the walls become more and more frequent. So the pressure which this causes becomes greater and greater, and is proportional to the degree of crowding (the **concentration**) of the molecules.

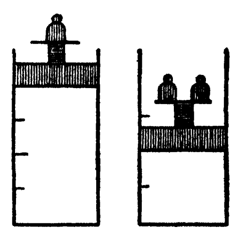


FIG. 59. Effect of Pressure on Volume.

There are two other points to be added. When we diminish the volume to one-half, we find from experience that the pressure

becomes exactly, or almost exactly, twice as great. This must mean that, although the particles are becoming crowded, they do not interfere with one another's motion, excepting of course where actual collision causes a rebound. Only in the absence of interference would doubling the number of molecules per unit of volume give exactly double the number of impacts on the walls. Hence the molecules must have practically no tendency to cohesion. Finally, the molecules must be supposed to move in straight lines between collisions.

Boyle's law therefore adds three more details concerning molecular behavior, namely, that the **crowding of the molecules** represents the *concentration of the material* and that the particles **move in straight lines** and **show almost no cohesion,** since *pressure* and *concentration are very closely proportional to one another.* Dalton's law of partial pressures emphasizes the fact that these rules hold not only for single gases, but for mixtures of gases.

How, now, can we account for *Charles' law* (p. 114), according to which an increase in volume (or in pressure, if the volume is kept constant) results from heating a mass of rapidly moving molecules? The action of a particle colliding with a surface is measured in physics in terms of its mass and its velocity (kinetic energy $= \frac{1}{2} mv^2$). It is evident that *heating* a cloud of molecules would not increase the mass of each, and it must therefore **increase the average velocity.**

Maxwell's Distribution Law. — It must be observed that all of the molecules in a homogeneous sample of gas at any given temperature have not the same velocity. If we examine closely the state of affairs at any instant, we find that some molecules have just suffered practically "head-on" collisions and consequently are momentarily almost stationary before the subsequent rebound, while others are temporarily travelling at a much higher velocity than their fellows as a result of hits from behind. The exact distribution of velocities at any moment has been worked out mathematically by Clerk Maxwell, and the formula representing this distribution is known as *Maxwell's distribution law.*

An illustration of this law is provided in Fig. 60, which shows in graphic form the distribution of velocities of oxygen molecules at 0° and 100° C. (273° and 373° Abs.). The velocity in meters per second is plotted horizontally; the vertical scale represents the fraction of the total number of molecules at any instant possessing velocities between n and $n+1$ meters per second. At 0° C., for

example, 0.2 per cent of the oxygen molecules have a velocity between 300 and 301 meters per second, while only 0.01 per cent have a velocity between 900 and 901 meters per second. As the temperature is raised, the most significant fact to note is that the fraction of molecules with velocities much greater than the aver-

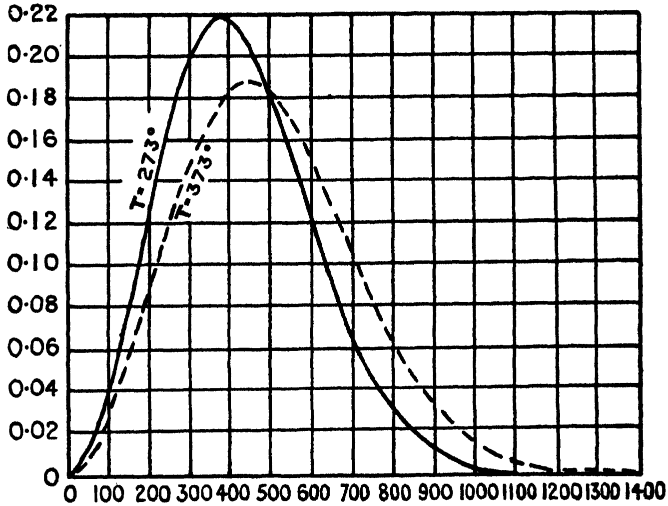


FIG. 60. Maxwell's Distribution Law.

age increases very rapidly. This is an important point to which we shall return later (p. 282).

Liquefaction of Gases: Critical Temperature.—We find by experiment, finally, that all gases can be *liquefied by sufficient cooling and compression.* This fact compels us to suppose that, after all, even gaseous molecules have *some* tendency to **cohesion.** This cohesion is, in general, scarcely perceptible so long as the gas is warm and under a low pressure, but it is possible, by careful measurement, to establish the fact that it does induce slight deviations from Boyle's law even under such conditions. Thus, 2 liters of oxygen at 1 atmosphere pressure, when subjected to 2 atmospheres pressure, give 0.9991 liter instead of 1 liter. The additional contraction of 0.0009 liter (0.9 c.c.) is due to the effect of cohesion when the molecules are thus crowded closer together. The gases which are more easily liquefied than is oxygen show greater effects. Thus, 2 liters of sulphur dioxide at 760 mm., when subjected to 2

atmospheres pressure, give 0.974 liter, showing a contraction due to cohesion of 26 c.c. These data refer to 0°. At lower temperatures the contractions due to cohesion become rapidly greater.

We can readily understand, therefore, that when the kinetic energy of the molecules is sufficiently reduced by cooling, and the molecules are brought sufficiently close together, the tendency of the molecules to cohere causes the gas to condense and assume the liquid form. In 1869 Andrews found that carbon dioxide could be liquefied at 0° by 38 atmospheres pressure, and at 30° by 71 atmospheres, but that above 31.35° it could not be liquefied by any pressure. He discovered that each gas has a **critical temperature,** as he called it. For carbon dioxide, this temperature can be observed by placing a heavy-walled glass tube (Fig. 61), half-filled with liquid carbon dioxide, in a beaker of water, and gradually raising the temperature of the latter. At 31.35°, the surface between the liquid and gas becomes hazy and vanishes. At this temperature the liquid state disappears, merging into the gaseous. When the temperature falls once more, the surface marking the boundary between liquid and gas reappears at 31.35°.



FIG. 61. Apparatus for Observing Critical Temperature.

The critical temperature of oxygen is —118°, of hydrogen — 240°, of sulphur dioxide 156°, and of water 374°.

Another Deviation from the Laws of Gases. A Perfect Gas. — It is also found by experiment that when a gas is already under very high pressure, and very closely packed, *an increase in the pressure does not produce as great a diminution in volume as Boyle's law leads us to expect.* This reminds us that we are **diminishing only the space between the molecules,** rather than the total volume of the gas. When, on severe compression, the volume occupied by the molecules themselves has become an appreciable fraction of the whole volume, additional compression affects only the residual fraction of the volume, and the contraction is smaller than Boyle's law would indicate. Thus, 200 liters of hydrogen, at 16° and under one atmosphere pressure, when subjected to 200 atmospheres pressure, give 1.134 liters, instead of 1 liter.

The last two effects (namely, those due to the tendency to cohesion of, and the space occupied by the molecules) are called **deviations** from the laws of gases. An imaginary gas, which exhibits

neither deviation, called a **perfect gas,** is often referred to in discussing the behavior of gases.

If the relatively incompressible space occupied by the molecules is called b, and that of the whole gas v, then the amended form of Boyle's law reads $p(v-b) = \text{constant}$. Similarly, if the cohesive tendency is taken into account, it is plain that its effect will become greater as v becomes smaller, *i.e.*, as the molecules are packed more closely together. It is in fact inversely proportional to the square of the volume. If it is expressed in the same units as the pressure by a, the total of the compressing tendencies becomes $p+\frac{a}{v^2}$. Hence Boyle's law, for constant temperatures, as amended by Van der Waals, reads $\left(p+\frac{a}{v^2}\right)(v-b) = \text{constant}$, a formula which describes the actual behavior of most gases with remarkable accuracy. Hydrogen alone, at ordinary temperatures, shows no excessive compressibility at low pressures. Thus, 2 liters of hydrogen at 760 mm., when subjected to 1520 mm. pressure, give 1.0006 liters, or 0.6 c.c. more than Boyle's law suggests.

It will be noted that the kinetic theory affords a mechanical explanation (*i.e.*, description in detail) of all the properties of gases, with the exception of the cohesion. It includes no machinery for explaining how the attractive forces between the molecules operate. This problem will be discussed in a later chapter (p. 492).

Summary. — We may now summarize the principal facts about gases in mass, appearing in italics above, with the corresponding features of the molecular relations, in heavy type, which we have added one by one.

Facts about Gases in Mass	Corresponding Relations of Molecules
Compressibility	Vacuum + molecules widely separated.
Diffusibility	Molecules in rapid motion.
Permeability	Empty space relatively large.
Non-settling	Molecules perfectly elastic.
Homogeneity	Molecules of any one substance closely alike.
Pressure	Due to impacts of molecules.
Boyle's law	Pressure proportional to concentration of the molecules. Molecules move in straight lines and, when widely scattered, show no tendency to cohesion or to repulsion.
Charles' law	Rise in temperature increases the velocity, and therefore the kinetic energy of the molecules.
Law of diffusion	Speed of molecules inversely proportional to square root of mass.
Gases can be liquefied, and show lower compressibility at high pressures.	Molecules do possess *some* tendency to cohesion, and do occupy an appreciable fraction of the space when pressure is very great.

History of the Kinetic-Molecular Theory. — This theory was first suggested by Daniel Bernoulli (1738), who explained by its means the pressure and compressibility of gases. Lomonossov (1748) developed the theory very completely and by means of it explained Boyle's law and the effects of changes in temperature. He also anticipated from the theory the existence of the second deviation from the law of gases (1749), a discovery usually credited to Dupré (1864). He likewise pointed out that there was no limit to the maximum velocity of a molecule, and therefore no upper limit of temperature, but that there must be a lower limit (the absolute zero) at which the molecules would be at rest (1744). This work was entirely forgotten, until attention was called to it in 1904 by Menschutkin.

Similar views were expressed by Waterston (1845), but were still so much ahead of the time that the committee of the Royal Society did not approve the paper for publication, and it was discovered in the archives of the society, long afterwards, by Lord Rayleigh. The development of the theory, so far as it applies to heat, is therefore credited to Joule (1855–60) and, in respect to all properties of gases, to Krönig (1856) and Clausius (1857), who knew nothing of the earlier work.

Exercises. — The text cannot be understood unless some problems involving the laws of gases are actually worked.

1. Reduce 189 c.c. of gas at 15° and 750 mm. to 0° and 760 mm.
2. Reduce 110 c.c. of gas at —5° and 741 mm. to 0° and 760 mm.
3. Convert 500 c.c. of gas at 25° and 700 mm. to 18° and 745 mm.
4. Reduce 250 c.c. of gas (standing over water) at 22° and 755 mm. to the dry condition and to 0° and 760 mm.
5. The density of a substance referred to air is 3.2. What is the density referred to hydrogen? What will be the volume occupied by 10 g. of the substance at 20° and 752 mm.?
6. What will be the relative rate of diffusion of the substance in question 5, (*a*) to hydrogen, (*b*) to air?
7. Convert the pressure of the atmosphere from mm. of mercury to (*a*) pounds per square inch, (*b*) tons per sq. ft. The density of mercury at 0° C. is 13.6, the average barometric height at sea level is 760 mm.
8. Reduce 100 c.c. of a gas at 750 mm. and 0° F. to 770 mm. and 68° F.
9. Why, in our lecture experiment on Charles' law (p. 114), do we need to adjust the mercury levels in the two tubes back to equality at the end of the experiment?
10. Using the same apparatus as in Exercise 9, the procedure is varied from that described on p. 114 as follows. When the gas has reached 100°, the side tube is *raised* until the volume is brought back to its original value at 20°. The difference in the mercury levels in the two tubes is then found to be 206 mm. The barometric height is 756 mm. What law has here been illus-

trated (pp. 115–6), and how does the observed value agree with the calculated?

11. Deduce algebraically the law illustrated in Exercise 10 by combining the laws of Boyle and of Charles, and express it in graphical form.

12. The volume of a given sample of gas at 748 mm. and 7° is 35.0 c.c. What will be its pressure when its volume is 34.0 c.c. and the temperature 18°?

13. The volume of a given sample of gas at 800 mm. and 23° is 150 c.c. The pressure is reduced to 700 mm. At what temperature would the gas occupy its original volume under this new pressure?

14. A tin can, containing a little water, is heated with a Bunsen burner until steam issues freely from its mouth. The flame is removed and the can is quickly stoppered. What happens when the can gets cool? Explain by means of the kinetic-molecular hypothesis.

15. The sun shines on an empty stoppered bottle, and the stopper is blown out. Explain by means of the kinetic-molecular hypothesis.

16. With the diffusion apparatus shown in Fig. 58 (p. 118), what will happen when the cylinder *H* is withdrawn? Explain by means of the kinetic-molecular hypothesis. (*Caution:* Two effects are to be observed, one after the other; be sure that you get both of them.)

17. One liter of hydrogen at 0° and 1 atm. is brought to 16° and 200 atm. pressure. What is the volume (p. 124)?

18. The following table shows the experimental densities and rates of diffusion of a number of gases, on the basis hydrogen = 1:

Gas	*Density*	*Rate of Diffusion*
Hydrogen	1	1
Methane	8	0.351
Nitrogen	14	0.265
Hydrogen sulphide	17	0.248
Carbon dioxide	22	0.212
Sulphur dioxide	32	0.177

Plot, on coördinate paper, a density-rate of diffusion curve. What is the equation for this curve? Compare the calculated rate of diffusion of each gas with the observed value.

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CHAPTER VIII

HYDROGEN

Having learned something of the properties of gases in general, and of oxygen in particular, we turn now to water, a substance as closely connected with our daily life as is air. We have seen (p. 95) that it is a compound of oxygen and hydrogen, and the latter element, therefore, may be taken up next. Hydrogen is of interest on its own account because it is often used in filling balloons, and nearly half (by volume) of ordinary illuminating gas is free hydrogen.

History. — Hydrogen, although discovered by Paracelsus in the sixteenth century, was confused with other combustible gases, and its independent nature was first established by Cavendish in 1766. Somewhat later (1781), the latter showed that hydrogen when it burned in the air gave water vapor, of which he condensed a large quantity to the liquid form. Taken in conjunction with Lavoisier's proof that oxygen was the active substance in the air (1777), this fact showed that water was a compound of hydrogen (Greek, ὕδωρ, water; γεννᾶν, to produce) and oxygen, and not a simple substance.

Occurrence. — Free hydrogen is found, mixed with varying proportions of other gases, in exhalations from volcanoes, in pockets found in certain layers of the rock-salt deposits, and in some meteorites. Surface air contains only an infinitesimal trace. The lines of hydrogen are prominent in the spectra of the sun and of most stars.

In combination, it constitutes about 11 per cent by weight of water. It is an essential constituent of *all* acids. It is contained also, in combination with carbon, in the components of natural gas, petroleum, coal, and all animal and vegetable bodies.

We have seen (p. 28) that, using the physical unit of weight, the element hydrogen stands ninth in order of plentifulness. But the *chemical* abundance of the elements should rather be reckoned by the relative numbers of atomic

weights which are available. When Clarke and Washington's numbers are recalculated to this percentage basis, hydrogen assumes a position more in harmony with its importance:

Oxygen	54.4	Aluminium	5.0	Iron	1.5
Silicon	16.1	Sodium	2.0	Calcium	1.5
Hydrogen	15.9	Magnesium	1.5	All others	2.1

Preparation by the Action of Metals on Cold Water. — To liberate hydrogen from water, it is necessary to use some element with which the oxygen of the water will combine even more energetically than with hydrogen, and to offer this element in exchange for the hydrogen.

The more active metals, such as potassium, sodium, or calcium, displace hydrogen rapidly from **cold water.** Potassium and sodium are lighter than water, and float on the surface. In the case of the former, so much heat is liberated that the hydrogen catches fire, and with neither metal is the experiment safe in the hands of a novice. Calcium sinks to the bottom, and acts rapidly, but not violently, so that the gas is easily collected (Fig. 62). In each case the metal displaces one-half only of the hydrogen in the water upon which it acts. The other products are the hydroxides of potassium, sodium, and calcium, respectively. The two former dissolve in the excess water, leaving a clear liquid when the metal is all gone, but may be recovered as white solids by evaporation. The calcium hydroxide (slaked lime) is dissolved only in part, and much of it may be seen suspended in the water after the action.

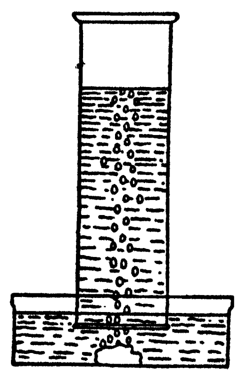


FIG. 62. Action of Calcium on Water.

To make the equation for each of the above reactions, we first write down the formulæ of the substances used and produced:

Skeletons:

$$K + H_2O \rightarrow KOH + H_2. \quad (1)$$
$$Na + H_2O \rightarrow NaOH + H_2. \quad (2)$$
$$Ca + H_2O \rightarrow Ca(OH)_2{}^* + H_2. \quad (3)$$

Next we must balance the equation, if necessary. That is, we must adjust it so that there are equal numbers of atomic weights (or atoms) of each element on both sides of the equation. This is done because, according to the law of conservation of mass, there must be the same quantity of each element

* The reason for writing the formula for calcium hydroxide $Ca(OH)_2$, rather than CaO_2H_2, will appear later (p. 147).

after the reaction as there was before it. On examining the third equation, for example, we note there is 2O, in the $(OH)_2$, on the right side and only O on the left. We therefore place a 2 in front of the H_2O, for we cannot get the additional oxygen excepting by using more water:

Balanced: $Ca + 2H_2O \rightarrow Ca(OH)_2 + H_2$.

The number of atomic weights of hydrogen has also been made equal by this procedure, and the equation is completely balanced.

The reader must practise the making and balancing of equations, until he can do it quickly. Equations (1) and (2) above will afford immediate practice. The text contains many equations, but more usually only the data required for making them (the formulæ of the substances) are given.

Displacement. — These actions, in which hydrogen is liberated, present us with a new — the third — variety of chemical change. Here **an element displaces** (either in whole or in part) **one of the elements from a compound,** setting it free, and **unites with the rest of the constituents of the compound.** Thus, calcium displaces part of the hydrogen, and unites with the oxygen and the rest of the hydrogen.

Hydrogen from Metals and Water at a High Temperature. — With **steam,** more inactive metals, metals like iron, zinc, and magnesium, when brought to a red heat, interact vigorously. The

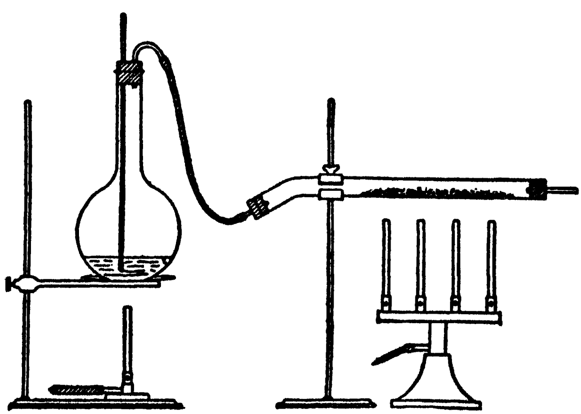


FIG. 63. Action of Iron on Steam

steam, generated in a flask, enters at one end of a tube containing the heated metal (Fig. 63), and the hydrogen passes off at the other. Since, at a red heat, all hydroxides, except those of potas-

sium and sodium, are decomposed into an oxide of the metal and water, as, for example, $Mg(OH)_2 \rightarrow MgO + H_2O$, the *oxides* are formed in this case:

$$Mg + H_2O \rightarrow MgO + H_2.$$

Iron, under the above conditions, gives the magnetic oxide Fe_3O_4 (compare p. 95).

Very inactive metals such as silver, gold, and platinum, which do not combine directly with pure oxygen, and even copper and mercury, which do, are all *unable* to form oxides and to liberate hydrogen when heated in steam.

Acids. — In making hydrogen in the laboratory, dilute acids are used almost exclusively. The most common acids are **hydrochloric acid** and **sulphuric acid.** The former is a solution of a gas, hydrogen chloride HCl, in water. The "pure concentrated" hydrochloric acid used in laboratories contains nearly as much of the gas (39 per cent by weight) as the water will dissolve. The "concentrated" sulphuric acid is an oily liquid, a compound of hydrogen, sulphur, and oxygen, to which chemists have given the name *hydrogen sulphate* H_2SO_4.

All the "dilute" acids contain 70 to 80 per cent of water. The water, as a rule, takes no part in the chemical changes in which the acids are concerned, and is therefore omitted from the condensed statements of their reactions.

The name "acid" is restricted to one class of substances having certain definite characteristics, which will be discussed in detail in a later chapter. It will suffice to mention at this point that *hydrogen* is the one essential constituent of all acids, that their aqueous solutions have a sour taste and change the color of litmus from blue to red, and that, in aqueous solution, also, their hydrogen is displaced, in whole or in part, by certain metals.

Preparation of Hydrogen by Displacement from Dilute Acids. — Every one of the metals which displace hydrogen from water will also displace it from dilute acids. The acids *must be diluted with water,* unless, like hydrochloric acid, they are already dissolved in water. The action is much more vigorous than that on water, so that the most active metals are not employed. Metals like zinc, iron, and aluminium serve the purpose. When excess of the metal is employed, hydrogen continues to be evolved until the acid present is all used up, and evaporation of the clear liquid which remains will then give in dry form the second product of

the reaction, namely, the compound resulting from the displacement of the hydrogen in the acid by the metal. Thus, with zinc and dilute sulphuric acid, zinc sulphate $ZnSO_4$ is produced:

$$Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2.$$

With aluminium and hydrochloric acid, the product is aluminium chloride $AlCl_3$:

Skeleton: $Al + HCl \rightarrow AlCl_3 + H_2.$

Balanced: $2Al + 6HCl \rightarrow 2AlCl_3 + 3H_2.$

For preparing small amounts of hydrogen, the apparatus (Fig. 64) is such that additional acid may be added through the thistle,

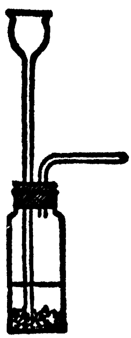


FIG. 64. Apparatus for Preparation of Hydrogen.

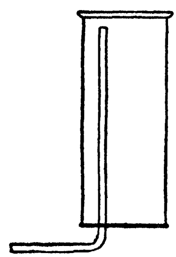


FIG. 65. Downward Displacement.

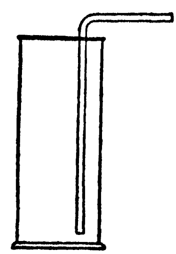


FIG. 66. Upward Displacement.

or safety tube, as desired. This avoids opening the flask and admitting air. The gas may be caught like oxygen over water or, being lighter than air, may be collected by **downward displacement** of the latter (Fig. 65). Heavy gases are collected by **upward displacement** of air (Fig. 66).

With a Kipp's apparatus (Fig. 67), the gas may be made on a large scale and its delivery can be regulated. When the stream of gas is shut off by the stopcock, the pressure of the gas, as it continues to be generated, drives the acid away from the metal and up into the globe above, so that the action ceases. Yet the action is ready to begin again the moment any portion of the stored gas is drawn off for use.

Contact of the zinc or iron with an inactive metal, like platinum or copper, forms an electrical couple (see p. 849) and hastens the interaction. For the same reason, commercial zinc, which contains traces of other metals, gives a steady evolution of hydrogen, while extremely pure zinc is almost inactive.

When water is *not* used along with the acid, the latter is either inactive or undergoes a different sort of chemical change. Perfectly dry (gaseous or liquefied) hydrogen chloride hardly interacts at all with zinc. Pure, concentrated sulphuric acid, on the other hand, although unaffected by zinc in the cold, is violently decomposed when heated. The action, however, is not a simple displacement of the hydrogen. The oxygen is removed from a part of the acid, and water and hydrogen sulphide are formed (see p. 403):

$$4Zn + 5H_2SO_4 \rightarrow 4ZnSO_4 + 4H_2O + H_2S.$$

The Proportions by Weight. — It may be well to remind ourselves that the weights of the various materials (implied in the equations) are proportionate to those obtained by laboratory measurements. It is always found that the total weight of the product is exactly equal to that of the materials used (p. 40). Also, that a given weight of the metal, say zinc, will always displace and liberate the same weight of hydrogen. Also, that the proportions by weight of the constituent elements in the compound produced are always the same (p. 42). If we place a weighed piece of zinc in hydrochloric acid, and wait until the zinc has all disappeared, we can then boil away the water and unused acid, and weigh the white, solid zinc chloride. We find that 65.37 grams of zinc always leave 136.29 grams of zinc chloride. The difference, 70.92, is the chlorine, and whatever weights we take, the proportion of zinc to chlorine in the zinc chloride is always in the ratio 65.37 : 70.92. The equation reads:

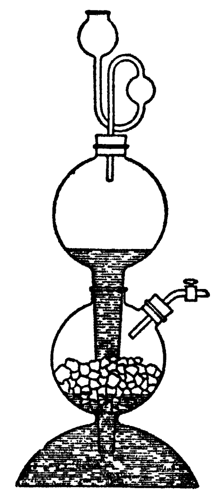


FIG. 67. Kipp's Apparatus.

$$Zn + 2HCl \rightarrow ZnCl_2 + H_2.$$

Chemically Equivalent Quantities. — It will be observed that 65.37 parts of zinc displace 2.016 parts of hydrogen, whether the acid used is sulphuric acid or hydrochloric acid. The proportion is, in fact, the same with every acid. Hence 65.37 parts by weight of zinc and 2.016 parts by weight of hydrogen are spoken of as **chemically equivalent** quantities. The quantities of the displacing and of the displaced element are in all reactions, indeed, regarded as chemically equivalent.

The term equivalent is applied also to the quantities *liberated by decomposition* of a compound, like the 401.2 parts of mercury and the 32 parts of oxygen (p. 42) obtained from mercuric oxide. It is likewise used of the proportions *combining* when chemical union takes place, as in the case of

phosphorus 124.16 parts and oxygen 160 parts (p. 95). The proportions of the elements in zinc chloride (p. 133) are also chemically equivalent.

Chemically equivalent quantities (or, simply, **equivalents**) of two substances are exact **quantities which enter into or result from a chemical reaction.**

Preparation of Hydrogen by Electrolysis. — If we dissolve *any acid* in water, and immerse the wires from a battery in the solution, bubbles of hydrogen begin to appear on the *negative* plate (the cathode) and rise to the surface. All the other constituents of the acid, whatever they may be, are attracted to the *positive* plate (the anode) and, therefore, do not interfere with the collection of pure hydrogen. An apparatus devised by Hofmann (Fig. 68) enables us to secure the hydrogen, which ascends on the right and accumulates at the top of the tube, displacing the solution. What may be liberated at the positive plate depends upon the acid used. With hydrochloric acid, it is chlorine; with sulphuric acid, oxygen comes off and sulphuric acid is regenerated.

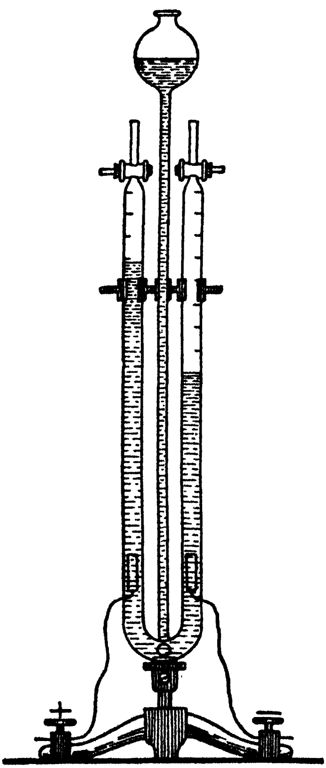


FIG. 68. Electrolysis of Dilute Sulphuric Acid.

Decomposition of a compound by the use of electrical energy is called **electrolysis.**

It is worth noting that pure acids and pure water, taken separately, are practically nonconductors of electricity. The fact that the *mixture* does conduct, concomitantly with the decomposition of the acid, is therefore highly suggestive (see Ionization).

It is commonly asserted that water is decomposed by a current of electricity. This is true in the sense in which we might say that a man can carry off a hill. He may eventually remove it, if you give him time. The action of electricity upon the purest water is exceedingly slow, on account of the very minute conductivity for electricity which it possesses. Common distilled water owes its appreciable capacity for conducting chiefly to traces of an acid, namely, carbonic acid, which it contains. Even when the water is saturated with carbonic acid, however, dilute hydrochloric acid has a conductivity of the order of many thousand

times greater. For our present purpose, therefore, water is declared to be a nonconductor. Yet, as we shall see, the conductivity of pure water, small as it is, has to be taken into consideration in certain cases (see Hydrolysis and Electromotive chemistry).

When a dilute solution of sulphuric acid is electrolyzed, the source of the hydrogen and the oxygen liberated is rendered obscure by the fact that the sulphuric acid itself contains both of these elements. When an aqueous solution of sodium fluoride NaF is employed, the same results are obtained, although the dissolved substance contains neither hydrogen nor oxygen. Neither the sodium nor the fluorine themselves can be liberated, however, because the hydrogen and oxygen of the water are more easily discharged and set free (see pp. 233, 359). This is a straight case of decomposing water by electrical energy.

Radicals.—In describing the chemical behavior of acids, we speak of the hydrogen as the **positive radical,** because in electrolysis it is attracted to the negative pole, and of the material combined with the hydrogen as the **negative radical,** because it is attracted to the positive pole. (In all circumstances, unlike charges of electricity attract, and like charges repel one another.) Thus in hydrochloric acid hydrogen is combined with the chloride radical, in sulphuric acid with the sulphate radical. The first is a simple radical, containing only chlorine (Cl), the second is a compound radical, containing sulphur and oxygen (SO_4). In many interactions the compound radicals move as units from one state of combination to another. Thus, when hydrogen is displaced from sulphuric acid by zinc, the negative radical SO_4 persists unchanged in zinc sulphate $ZnSO_4$. This compound also, in water solution, is decomposed by electrolysis, and the fact that the zinc is attracted to the negative plate indicates that zinc, like hydrogen, is a positive radical.

Compounds, such as hydrogen chloride and zinc sulphate, whose positive and negative radicals are attracted to the negative and positive poles of a battery when an electric current is passed through their aqueous solutions, are called **electrolytes** or **polar compounds** (compare p. 70). The migration of the two radicals of a polar compound towards the oppositely-charged electrodes is obviously connected with their acquisition of positive and negative electrical charges through loss and gain of electrons in the process of combination. The lack of any *specific* union between the two radicals constituting such compounds has already been discussed (p. 69), and their independent behavior in electrolysis furnishes, indeed, one of the main arguments against the existence here of definite molecular units. Other arguments will be adduced later (Chapter XVIII).

Explanation of Electrolysis. — When we immerse two wires, each connected with one of the poles of a battery, in a water solution of a polar compound, such as hydrochloric acid HCl, what happens is as follows. Because of chemical reactions occurring inside the battery, the negative wire or cathode is teeming with an excess of electrons, while the positive wire or anode has lost electrons and seeks to make up its deficiency. Of course, if the wire continued all through the solution, a steady stream of electrons would pass along it in order to equalize matters. In the absence of such a connecting wire, the positive and negative radicals of the acid do their best to assist. The positive radicals here are hydrogen atoms, each of which has lost an electron and has thereby become a hydrogen ion H^+. The negative radicals are chlorine atoms, each of which has acquired an electron and has thereby become a chloride ion Cl^-. The hydrogen ions are attracted to the negative pole in the expectation of recovering there the electrons which they have lost, while the chloride ions migrate to the positive pole with the purpose of delivering their extra electrons at the spot where they are urgently needed. Two orderly processions of ions, moving in opposite directions, proceed therefore through the solution towards the electrodes. Ions (Greek, *going*) derive their name from this fact.

The rest is easily understood. When a hydrogen ion reaches and touches the negative electrode, it gains an electron, and the result is an ordinary atom of hydrogen. The atoms of free hydrogen unite to give molecules (H_2) and these form bubbles of the gas. Simultaneously the chloride ions lose electrons at the positive electrode, and the atoms of free chlorine unite to give molecules (Cl_2).

Other Ways of Preparing Hydrogen. — For special purposes, hydrogen may be made by boiling an aqueous solution of sodium hydroxide with aluminium turnings, when sodium meta-aluminate is formed; also by heating powdered zinc and solid sodium hydroxide, the product being sodium zincate. These reactions will be discussed later, under aluminium and zinc respectively.

$$2Al + 2NaOH + 2H_2O \rightarrow 2NaAlO_2 + 3H_2.$$
$$Zn + 2NaOH \rightarrow Na_2ZnO_2 + H_2.$$

Hydrogenite — a mixture of ferrosilicon and sodium hydroxide (see p. 658) — and **hydrolyte** or calcium hydride (see p. 721) are also occasionally employed in the preparation of hydrogen.

Sources of the Hydrogen of Commerce. — Zinc is too expensive a substance to use in the preparation of hydrogen in large quantities for commercial purposes. We realize this when we note that 65 parts of zinc will liberate only 2 parts of hydrogen from hydrochloric or sulphuric acid, so that with 1 lb. of zinc we obtain only one-half ounce of the gas. Different sources are used in different localities and countries.

A limited quantity is obtained as a by-product in the electrolysis of an aqueous solution of common salt (sodium chloride), in connection with the manufacture of caustic soda (sodium hydroxide, p. 234). The hydrogen is collected and compressed in steel cylinders.

In some circumstances, the method of passing steam over heated iron is used (p. 130).

The largest amount of commercial hydrogen, however, is made by purification of water-gas, which is a mixture of hydrogen and carbon monoxide (p. 570). This, and still other processes, involve substances and reactions which we have not yet encountered, and will be mentioned at the appropriate points.

Preparation of Simple Substances. — There are two general sources from which we **obtain simple substances.** **If the element occurs uncombined in** nature, as sulphur and gold do, it is only necessary to free it from foreign materials (impurities) with which it is mixed. If no such supply exists, or if the purification is difficult, then some compound, natural or artificial, is decomposed.

The **liberation of an element from combination** is likewise effected in two ways: (1) The compound may be forced apart by the application of energy, usually in the form of heat or electrical energy. Thus, heat was employed to liberate oxygen (pp. 23, 89–91). Electrical energy, however, was used in one way of obtaining hydrogen (p. 134), since readily obtainable compounds which, when heated, give hydrogen as the only gaseous product, are unknown. Electrical energy may be used also to liberate any metal.

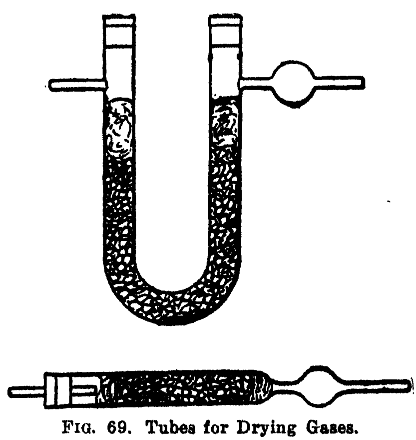


FIG. 69. Tubes for Drying Gases.

(2) The other general method of setting an element free is to offer to the other constituents of the compound some substance with which they will unite. This plan is used in liberating hydrogen from acids and from water (pp. 129–32).

In selecting our source, we are naturally influenced by the cost of the material, as well as by the ease of the process. Thus, gold oxide yields oxygen by the application of very little heat, but it is extremely expensive. Quicklime is very cheap, but does not give up its oxygen even at the temperature of the electric arc. As a laboratory source of hydrogen, any acid may be used, theoretically, but the cheapest and commonest acids (hydrochloric acid and sulphuric acid) are actually employed.

Purification of Gases. — Hydrogen made in any of the above ways is impure (p. 8). As made by all the laboratory methods mentioned, a good deal of water vapor is mixed with it. Other impurities, like hydrogen sulphide and arsine, come from the action of the acid on foreign materials in the zinc (p. 132). Some of the acid, if it is volatile, will also be taken over with the gas. When the object for which the gas is being made demands it, we must know what the impurities to be expected are, and take proper means of removing them.

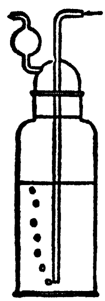


FIG. 70. Gas Washing Bottle.

Gases are freed from aqueous vapor (dehydrated) by means of calcium chloride or concentrated sulphuric acid, which greedily absorb moisture. The former is used in granulated form in straight or bent tubes (Fig. 69). The latter is applied by saturating pieces of pumice-stone with the acid and filling similar tubes with the fragments. Or the acid may be placed in a gas washing bottle (Fig. 70). For extremely complete drying, a tube may be filled with phosphoric anhydride P_2O_5 sifted upon glass beads or glass wool. Forethought must be used to avoid a drying agent which will interact with the gas. The longer the gas remains in contact with the drying agent, the more perfect, up to a certain limit, is the purification effected. In all cases, the stream of gas must pass slowly.

Particles of liquid or solid matter are always carried along by freshly made gases. These will pass with the gas through sulphuric acid without being affected. A plug of cotton or of glass wool in some part of the tubing is required to arrest them.

Physical Properties of Hydrogen. — Some of these may be given in tabular form:

Colorless	Crit. temp., —240°
Tasteless	Sp. ht. (gas, const. press.), 3.4
Odorless	Boiling-point, —252.5°
Density (air = 1), 0.0695	Melting-point (58 mm.), —260°
Wt. of 1 l., 0.08987 g.	Sol'ty in Water, 1.8 vols. in 100 (20°)

Air is thus 14.5 times heavier, hence hydrogen may be poured upwards (Fig. 71) and is used for filling balloons.

The specific heat of hydrogen under constant pressure is about seventeen times that of oxygen (0.2). Its thermal conductivity is greater than that of any other elementary gas. A wire, raised to incandescence in air by means of an electric current, cannot be kept at a red heat, even, by the same current in hydrogen. If a heavier current is applied, much of the heat is used, not merely to

increase the velocity of the hydrogen molecules which strike the glowing wire, but also to decompose them into atoms (see Chap. XI).

Hydrogen was first liquefied in visible amounts by Dewar (1898). The liquid is colorless and, when allowed to evaporate rapidly under reduced pressure, freezes to a colorless solid. All other gases, except helium, solidify easily when led into a vessel surrounded by liquid hydrogen.

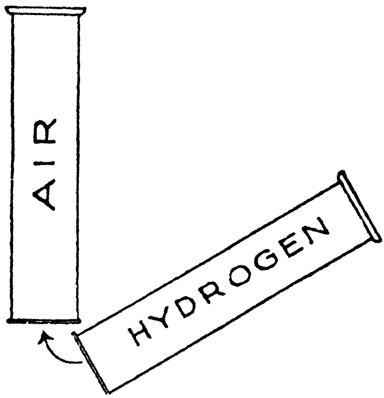


FIG. 71. Pouring Hydrogen Upwards.

Hydrogen is adsorbed, or occluded, for the most part in a purely mechanical way, by many metals, such as iron, platinum and palladium (see p. 816).

Chemical Properties. — Hydrogen, delivered from a jet, burns in air or pure oxygen. A cold vessel held over the almost invisible blue flame condenses to droplets of water the steam that is produced (Fig. 72). When hydrogen and oxygen are mingled in a suitable burner (Fig. 73), although the flame gives little light, it is exceedingly hot. Platinum melts in it easily and an iron wire burns brilliantly. In a closed space it produces a temperature of over 2500°. When the flame is allowed to play on a piece of quicklime, the latter becomes white-hot at the spot where the flame meets it. This result is called a **calcium light or lime light.**

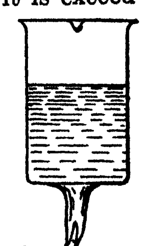


FIG. 72. Burning Hydrogen in Air.

When hydrogen and oxygen are mixed, the chemical action is very slow at ordinary temperatures, *no perceptible amount of union occurring in a period of five years.* If the mixture is sealed up and kept at 300°, after several days a small part is found to have combined to form water. At 500°, hours are required before the union is com-

plete. At 700° the combination is almost instantaneous. Hence contact with a body at a bright-red heat is required actually to explode the mixture.

Finely divided platinum (see p. 817), when held in the cold mixture, hastens the otherwise vanishingly slow union in the part of the gases in contact with it. The heat of their union raises the temperature of the platinum to a white heat and this causes explosion of the whole mass of gas. The platinum is simply a catalyst (p. 103) and remains itself unaffected. The same explanation applies to self-lighting gas jets and to some pocket cigar lighters.

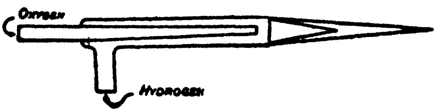


FIG. 73. Oxy-hydrogen Burner.

Hydrogen unites directly with a minority only of the simple substances. It combines readily with oxygen, chlorine, fluorine, and lithium (an active metal), and more slowly with a few others.

Hydrogen also unites with oxygen and chlorine, even when these elements are already combined with the less active metals. Thus, when one of the oxides of copper or of iron is heated in a tube through which hydrogen flows, the latter combines with the oxygen to form water, and the metal is liberated:

$$CuO + H_2 \rightarrow H_2O + Cu.$$
$$Fe_3O_4 + 4H_2 \rightarrow 4H_2O + 3Fe.$$

These interactions are classed, by mechanism, as **displacements.** The second one, it will be noted, is the reverse of the reaction between steam and iron (p. 131). This reversal, as in the case of barium peroxide (p. 90), is brought about by a change in the *conditions,* as will be discussed in detail later (p. 177).

Reduction. — The removal of oxygen from a compound by its union with some other substance is called **reduction** and the substance (in the foregoing instance, hydrogen) is called a **reducing agent.** Carbon, in the form of coal or coke, is the agent of this kind most commonly used in chemical industries. The term reduction is also applied to some other chemical actions, in which oxygen is not concerned. In all cases, however, reduction is the opposite of oxidation (p. 97).

An Inapt Use of the Word "Affinity" in Explanation of Chemical Actions. — Speaking without reflection, one might be tempted to "explain" actions like the reduction of magnetic oxide of

iron, just mentioned, by saying that the hydrogen has a greater tendency to unite with oxygen, or has a *greater affinity* for it, than has iron, and therefore removes the oxygen from combination with the latter. Plausible as this statement seems, it would be in many cases, as here, quite incorrect. Under the modes of preparing hydrogen, we spoke of the action of steam upon iron (p. 130), which gives the equation: $3Fe + 4H_2O \rightarrow Fe_3O_4 + 4H_2$. To use consistently this handy method of explaining chemical change by the help of the word "affinity," we should have to say here that the hydrogen has a *less affinity* for the oxygen than has iron, and therefore hydrogen is set free and oxide of iron is formed. It will be seen that this statement is in direct contradiction to the one made above. Both cannot be true. The fact is that both are based upon an assumption which is incorrect — the assumption, namely, that the displacement of one element by another is always an evidence of the greater affinity of the latter. The correct explanation of seemingly contradictory actions like these will be given later (see p. 177).

The action of catalytic agents is itself a refutation of this blundering assumption. Putting a little platinum in a mixture of oxygen and hydrogen cannot add to the energy contained in these substances, and cannot therefore increase their intrinsic tendencies to unite. Yet in its presence an almost nonexistent action becomes suddenly explosively violent. There are other factors, often far more potent than affinity, which determine the direction and speed of many chemical changes (see Chemical equilibrium).

In this connection, it is worth noting that, while increasing the speed of a train or a ship requires a great addition to the energy expended, and is very costly, increasing the speed of a chemical change requires the expenditure of no energy whatever. The employment of a couple (p. 132) or a catalytic agent adds nothing to the energy the separate bodies possessed before they were mixed. And the catalytic agent is recovered *unchanged* and as efficient as ever at the end. The increased speed in the formation of the products is thus obtained gratis. The contact method of making sulphuric acid (see p. 420) illustrates how commerce has taken advantage of this fact.

The Speed of Chemical Actions: a Means of Measuring Activity. — One means of measuring the relative chemical activities (p. 99) of several substances, is to observe the speed with which they undergo the same chemical change. Thus we may compare the activities of the various metals by allowing them separately to interact with hydrochloric acid and collecting and measuring the hydrogen liberated per minute by each. It will be seen, even in the roughest experiment, that magnesium is very much more active than iron. The comparison must be made with such precautions, however, as will make it certain that the conditions under

which the several metals act are all alike. Thus, in spite of the heat evolved by the action, means must be used, by suitable cooling, to keep the temperature at some fixed point during all the experiments, for all actions become more rapid when the temperature rises (p. 100). Again, pure materials must be used, as an impurity in one metal might act as a contact agent and modify the natural speed of the action (p. 132). Still again, the pieces of the various metals must be arranged so that equal surfaces are exposed to the acid in each case. Equal weights of zinc will ultimately displace equal weights of hydrogen; but if one of them is in the form of foil while the other is a cylinder, the former, although it will not last so long, will liberate more hydrogen per minute. Finally, the portions of hydrochloric acid must contain the same percentage of hydrogen chloride in each case. When these and other precautions have been taken, a true comparison of the relative activities of the metals with respect to this particular action may be made. It is found that the order in which this comparison places the metals is much the same as that in which they are placed by a study of other similar actions. A single table suffices, therefore, for all purposes (see next section).

The Order of Activity of the Metals. — We employ metals so frequently in chemistry, that we must at once become familiar with the key to the main differences in their behavior. The order of their activity explains these differences, as well as many other facts. In the adjoining list, the most active metals are at the top. Hydrogen is not a metal, but is included because chemically it resembles the metals. All the metals above hydrogen displace this element from dilute acids (and, with more difficulty, from water); those below it do not.

ORDER OF ACTIVITY. METALS.

Potassium
Sodium
Calcium
Magnesium
Aluminium
Manganese
Zinc
Chromium
Iron
Nickel
Tin
Lead
Hydrogen
Antimony
Bismuth
Copper
Mercury
Silver
Platinum
Gold

The first displaces the hydrogen from water so violently that the gas catches fire, the second displaces it vigorously, the third less vigorously. Magnesium requires hot water and iron superheated steam. Copper and the metals following it do not liberate hydrogen from water.

Again, the upper metals act too violently on dilute acids, and zinc is used to prepare the gas. Copper and the metals following it do not displace hydrogen from dilute acids.

Still again, we recall the fact (p. 95) that, when we

heat metals in pure oxygen, the last three do not become oxidized at all. Those preceding silver do combine with pure oxygen — mercury with difficulty, and the others more and more vigorously as we ascend the list. On the other hand, if we start with the oxides of all the metals, we find that those at the foot of the list, up to and including mercuric oxide, lose all their oxygen when heated over a Bunsen flame, leaving the metal. If we heat the oxides, and also pass hydrogen over them, the oxygen is easily removed from all the oxides up to and including those of iron, leaving in each case the metal. Oxides of metals above iron in the "order of activity," however, are very stable, and cannot be reduced by hydrogen. Thus, in general, the more active metals form the most stable compounds (compare p. 264).

Other facts of a similar nature will be mentioned as we encounter them. Meantime, it may be noted that the metals found uncombined in nature in large amounts are those following hydrogen. Those preceding hydrogen, if liberated, since they all displace hydrogen from acids, would act slowly on natural waters containing carbonic acid (p. 171), and so would pass into combination. Hence those preceding hydrogen are found free only in exceptional cases, such, for example, as the metallic iron of which meteorites often consist. Again, the metals known to have been first used by the human race were gold and silver. In the "bronze age" means of liberating copper from its ores had been discovered. Lead, tin, and iron came later. The list, read from the bottom up, gives therefore, roughly, the historical order in which the metals came into use.

Industrial Hydrogen and Recent Developments. — Many of the minor uses of hydrogen have been mentioned in the preceding sections. Much more important industrial applications have recently been developed, however, such as the synthetic production of ammonia (p. 507), the hydrogenation of oils (p. 634), the hydrogenation of coal (p. 626), and atomic-hydrogen arc welding (p. 510). These will be referred to in detail in subsequent chapters.

The discussion of several recent developments of primary theoretical significance in the chemistry of hydrogen — such as its dissociation into atoms at high temperatures, the existence of two types of hydrogen molecule (ortho- and para-hydrogen), and the discovery of heavy isotopes of hydrogen (deuterium and tritium) — will also be postponed at this stage for more extended treatment at appropriate points later.

Exercises. — 1. Make equations for reactions in which hydrogen is liberated by the action of: (*a*) hydrochloric acid and magnesium, giving $MgCl_2$, (*b*) steam and zinc, giving ZnO.

2. Make equations to represent, (*a*) the reduction of lead dioxide PbO_2 by hydrogen; (*b*) the actions of aluminium upon cold water and upon steam at a red heat.

3. Which are the components (p. 8) of dilute sulphuric acid and which are the constituents of sulphuric acid?

4. Name three varieties of chemical change (pp. 15, 23, 130) and explain the difference between them. To which of the three varieties of chemical change does the action of hydrogen on magnetic oxide of iron (p. 140) belong?

5. What weight of hydrogen would be obtained by the action of excess water on (*a*) 100 g. potassium, (*b*) 100 g. calcium? What weight would be obtained by the action of excess steam on (*a*) 100 g. magnesium, (*b*) 100 g. iron?

6. A liter of air at 0° and 760 mm. weighs 1.293 g.; a liter of hydrogen under the same conditions weighs 0.08987 g. A rubber balloon, weighing 5 g., is inflated with hydrogen. Assuming that the gas inside is under the same pressure as the air outside (760 mm.), calculate to what volume the balloon must be inflated so that it will just float at 20°.

7. Using the data in Exercise 6, calculate what weight the same balloon will lift, if it is inflated to a volume of 10 liters with hydrogen, the temperature being 27° and the pressure 750 mm.

8. From the condensed statements given in the text, tabulate the equivalent quantities of (*a*) iron and oxygen (p. 95), (*b*) hydrogen and oxygen (p. 95), and (*c*) iron and hydrogen (p. 140). What conclusion may you draw from your figures? Is this conclusion always justified (p. 17)?

9. What weight of zinc must be added to excess hydrochloric acid to produce 22.4 liters of hydrogen at 0° and 760 mm.?

10. Three separate portions of magnesium, each weighing 10 g., are taken. One is treated with excess steam, the second with excess hydrochloric acid, the third with excess sulphuric acid. What weight of hydrogen is obtained in the first case (p. 131)? What weights of hydrogen are obtained in the second and third cases (see p. 148)?

11. A sample of hydrogen, standing over water at 68° F. and 740 mm. pressure, occupies 500 c.c. The conditions are changed to 50° F. and 750 mm. pressure. What is the new volume (Appendix IV)?

12. What is the weight of pure hydrogen present in the sample mentioned in Exercise 11?

13. Tabulate as many uses of hydrogen as you can remember, and discuss each in relation to the physical and chemical properties of the element (see p. 86).

14. Devise *two* distinct methods for determining the chemically equivalent quantities of (*a*) magnesium and oxygen, (*b*) iron and hydrogen.

READING REFERENCES

Kendall; At Home among the Atoms, Chapter IX.

Alembic Club Reprints, No. 3. Experiments on Air (Cavendish).

CHAPTER IX

VALENCE

Equivalence and Valence. — If the equations showing displacement of hydrogen by a metal be now reëxamined, a peculiarity will be observed which we have thus far omitted to discuss. When sodium and calcium (p. 129) act upon water, one atomic weight of the former displaces one atomic weight of hydrogen, but one atomic weight of the latter displaces twice as much hydrogen. Again, each atom of zinc (p. 132) displaces two atoms of hydrogen, but each atom of aluminium displaces three. Assuming, for simplicity, that we allow these metals all to act upon dilute hydrochloric acid, the equations are:

$$2Na + 2HCl \rightarrow 2NaCl + H_2.$$
$$Ca + 2HCl \rightarrow CaCl_2 + H_2.$$
$$Zn + 2HCl \rightarrow ZnCl_2 + H_2.$$
$$2Al + 6HCl \rightarrow 2AlCl_3 + 3H_2.$$

Interpreting this, we perceive that each atom of aluminium, for example, displaces 3 atoms of hydrogen, *because it is able to combine with 3 atoms of chlorine,* and so incidentally liberates the hydrogen formerly united with these 3 atoms of chlorine. The atomic weight of aluminium is thus *equivalent to* (equal in chemical value to) 3 atomic weights of hydrogen (compare p. 133) and, since it combines with 3 atomic weights of chlorine, it is also equivalent to 3 atomic weights of this element. Each atom of sodium, however, can combine * with only 1 atom of chlorine, and so releases only 1 atom of hydrogen. Now this is not a rule confined to these reactions, but represents a general chemical property of each element, and a property which we shall find it most useful to investigate.

* The word *combine* is used here in a statistical sense only. As we saw in an earlier chapter, no sodium atom in a crystal of sodium chloride is actually united with any single specific chlorine atom. Even a crystal of microscopic size, however, contains myriads of sodium atoms and chlorine atoms in equal numbers, and, for convenience, we shall continue to express this fact by the empirical formula NaCl.

The *chemical property* referred to is called **valence.** The valence of an atom of hydrogen or of chlorine is, for reasons which will appear presently, made the unit. An atom of sodium is said to be **univalent,** one of calcium **bivalent,** one of aluminium **trivalent.** The formula H_2O shows the atom of oxygen to be bivalent, because it unites with two atoms of hydrogen.

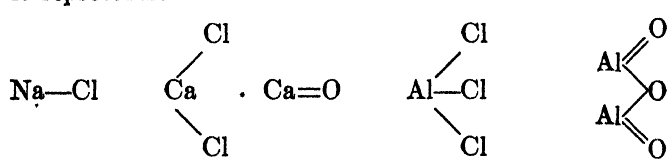
Stated briefly, **the valence of an element is the number of atoms of hydrogen, or of chlorine, which one atom of the given element combines with or displaces.**

Marking the Valence. — Until we have become familiar with the valence of each element, it is advisable to mark the valences in a special way: Na^{I}, Ca^{II}, Al^{III}, O^{II}, Zn^{II}, Cl^{I}.

As we should expect, a bivalent atom can combine with two univalent atoms, *or with one bivalent atom,* and so forth. Thus we have the compounds of oxygen: $Na_2{}^{I}O^{II}$, $Ca^{II}O^{II}$, $Al_2{}^{III}O_3{}^{II}$, $Zn^{II}O^{II}$, $Cl_2{}^{I}O^{II}$.

The rule is that **the quantities of two elements which combine must have identical total valence.** Thus, Ca^{II} has the valence two, and so does O^{II}. Again, $Al_2{}^{III}$ has a total valence of 2×3 $(= 6)$ and so has $O_3{}^{II}$ $(3 \times 2 = 6)$.

Frequently the valence is marked by means of lines, the number of lines pointing towards a symbol indicating the valence of the atom it represents:



This procedure, though useful in a way, has certain dangers, since the tendency naturally arises to regard such a "graphic formula" as giving an actual picture of the arrangement of the atoms in the molecule. This, of course, no representation on paper can possibly do, since a compound is a three dimensional affair, and we have already seen in our study of crystals (p. 68) that the picture of sodium chloride is much more complex than plain Na-Cl.

How to Learn the Valence of an Element. — To find out the valence of an element, we need only to determine by means of a quantitative experiment (p. 78) the formula of one characteristic binary compound of the element, containing another element of known valence. Thus, what is the valence of carbon? Its most

stable oxide (p. 95) is CO_2. The total valence of the two oxygen atoms here is $2 \times 2 = 4$. Carbon C^{IV} is therefore *quadrivalent.* Hence its corresponding chloride must be $C^{IV}Cl_4{}^{I}$ (carbon tetrachloride), and its simplest compound with hydrogen $C^{IV}H_4{}^{I}$ (methane, composing a large part of natural gas). When carbon combines with a trivalent element, equivalent amounts of each element must normally be used, as in $Al_4{}^{III}C_3{}^{IV}$ (aluminium carbide), where $Al_4{}^{III}$ and $C_3{}^{IV}$ contain 3×4, or 12 units of valence each.

Again, when we know the formula of sodium iodide to be $Na^{I}I$, or that of hydrogen iodide to be $H^{I}I$, we infer that iodine is *univalent.* The formula of silica (sand) $SiO_2{}^{II}$ shows silicon to be *quadrivalent,* and indicates that the chloride must be $SiCl_4$.

Valence of Compound Radicals. — What we have said so far applies only to compounds of not more than two elements — so-called **binary compounds.** We cannot, by mere inspection, tell the valences in a compound of three or more elements, like sulphuric acid H_2SO_4. But we have seen (p. 135) that the acids and other polar compounds behave as if composed of two radicals: H(Cl), $H_2(SO_4)$, that is, of two groups — one positive and one negative — which move as wholes in chemical reactions. Hence we can assign a valence to a compound radical *as a whole.* Thus the negative radical $(SO_4)^{II}$ is evidently bivalent, as a whole, because it is united with $2H^{I}$. Na(OH) and $Ca(OH)_2$ show the negative radical **hydroxyl** (OH), present in hydroxides or bases (p. 174), to be univalent.

The positive radical of a polar compound is almost always a metal. Hydrogen, it will be noticed, is considered to fall into the class of metallic elements according to this scheme (compare p. 142). Other elements commonly regarded as non-metallic may enter into a positive radical, but only in groups which imitate metals in their properties, such as the ammonium group NH_4. The negative radical of a compound is sometimes a single non-metal and sometimes a group of elements, such as the sulphate group SO_4. The valence of the positive part must necessarily be equal to the valence of the negative part, and you will find this simple rule of great service in writing down formulæ correctly. Thus, for example, you can work out the formula of aluminium sulphate (a salt used extensively in baking-powders, in paper-making, in water purification, and in dyeing) from what you know already in the following way. The valence of aluminium is three, since one atom of aluminium combines with three atoms of chlorine and displaces three atoms of hydrogen. The valence of the sulphate radical is two, since it is combined with two atoms of hydrogen in sulphuric acid H_2SO_4. The simplest possible formula for aluminium sulphate is, consequently, $Al_2(SO_4)_3$. We write $(SO_4)_3$ in this formula rather than S_3O_{12} in order to emphasize the continued presence

of the SO_4 group, just as in the formula for slaked lime $Ca(OH)_2$ (see p. 129) we preserved the identity of the hydroxyl group. In fact, substances which commonly interact as if the radicals were single elements, we regard as binary compounds.

A table of the valences of the more important elements and radicals will be found at the end of this book (Appendix V).

The reader must make a special effort always to learn the valences of each element and radical, and always to use them in making formulæ.

The reader must also always *check every formula he writes from memory,* to make sure that it is correct. Thus, if he thinks the formula of zinc nitrate is $ZnNO_3$, he must count the valences, $Zn^{II}(NO_3)^{I}$. Evidently, the *correct* formula is $Zn(NO_3)_2$.

Positive and Negative Valence. — We can, at this point, begin to analyze our conception of valence a little more closely. We have seen that polar compounds behave as if they comprise positive and negative radicals which are, in a sense, independent of one another (p. 135). We have also seen that such compounds are formed as the result of the transfer of loose electrons from the positive to the negative units (p. 69). Combining these ideas with what we have learned in the present chapter, we can distinguish two types of valence — **positive valence,** which represents the number of electrons that an atom (or radical) loses in entering into combination, and **negative valence,** which represents the number of electrons that an atom (or radical) gains. Hydrogen normally loses one electron to give the positive ion H^+; chlorine normally gains one electron to give the negative ion Cl^-. These two elements, consequently, afford us a convenient basis for determining the valences of other positive and negative radicals. Thus, in sodium chloride, which has the empirical formula NaCl, the univalent character of the positive radical and its loss of a single electron to a chlorine atom is indicated by the formula Na^+ for sodium-ion (p. 70). In magnesium chloride, on the other hand, with the empirical formula $MgCl_2$, each atom of Mg has lost two electrons to two chlorine atoms, and furnishes the bivalent magnesium-ion Mg^{++}. Similarly, zinc-ion (bivalent) is Zn^{++}, aluminium-ion (trivalent) Al^{+++}, and so on.

In the same way, for negative radicals, the fact that the sulphate group SO_4 has gained two electrons in combining with *two* sodium atoms in Na_2SO_4 or with *one* magnesium atom in $MgSO_4$ is recognized by the formula for sulphate-ion $SO_4^{=}$. The chloride ion Cl^- and the hydroxyl ion OH^- are univalent, the phosphate ion $PO_4^{\equiv}$ (derived from phosphoric acid H_3PO_4) is trivalent.

As we have stated before, loss of electrons is characteristic of

metallic elements, and gain of electrons is characteristic of non-metallic elements. Besides the two kinds of valence — positive and negative — which result therefrom, there is, however, a third kind of valence, called **co-valence,** which we must not omit to examine.

Co-Valence. — We have already encountered a number of common compounds which are not of a polar character. A few examples may be mentioned to make this clear — for instance, benzene C_6H_6 (p. 71), naphthalene $C_{10}H_8$ (p. 71), phosphorus pentoxide P_2O_5 (p. 95), and carbon disulphide CS_2 (p. 21). These compounds do not conduct an electric current under any circumstances (hence they are styled *non-polar*), and there is no justification for splitting their formulæ up into positive and negative parts. Why should these compounds differ so decidedly from those we have hitherto examined? If we look at their formulæ we notice at once that they are composed entirely of non-metallic elements. Now under such conditions, with no atoms present disposed to lose electrons, there is no *transfer* of electrons from one atom to another; combination into a molecule consists instead in the *sharing* of electrons between atoms. The electrons are shared in pairs in every case, each of the atoms concerned generally contributing one of the pair. The **co-valence of an element** represents, then, the *number of pairs of electrons which an atom of that element can share with atoms of other elements.* In a later chapter we shall scrutinize the three kinds of valence — positive, negative, and co-valence — more intently, and we shall discover that the valence number in each case does not vary in a casual way from element to element, but follows a simple and definite scheme.

Polar and Non-polar Compounds. — In the course of the above discussion, we have grouped compounds into two distinct classes, *polar compounds* which conduct the electric current in consequence of an electron transfer between their constituent radicals, and *non-polar compounds* which do not conduct the electric current, since electrons are merely shared and no charged radicals are formed. Strictly speaking, however, the distinction between polar and non-polar compounds is not fundamental, but one of degree only. No substance is a perfect non-conductor of electricity and no substance exhibits, under any practical conditions, its maximum possible conducting capacity. In fact, a list of compounds could be drawn up, starting with benzene and ending with fused sodium chloride, in which there is a gradual and continuous transition from

very poor conductance to almost perfect conductance. Even the same compound behaves differently according to the environment in which it finds itself. Thus pure sulphuric acid H_2SO_4 is a liquid which is an extremely poor conductor. Pure water H_2O is also a liquid which is practically a non-conductor. A mixture of water and sulphuric acid, however, conducts the electric current excellently.

We can understand all this by recognizing the fact that an electron is not *forced* to pass over completely from one atom to another or else be shared equally by the two; it may choose to follow an intermediate course. In no non-polar compound, probably, are pairs of electrons held in common between two atoms so impartially that they will not tend, to some (even though very small) extent, to associate themselves with one atom rather than with the other. In the same way, in no polar compound does an electron pass from one atom to another irrevocably and irretrievably; the attractive forces induced between neighboring and oppositely charged atoms must tend, to some (even though very small) extent, to pull it back occasionally into a straddling position.

This is one of many instances in chemistry where we find it convenient to classify substances or reactions into various groups, without being able to draw any definite boundaries between the groups. Our classification of elements into metals and non-metals is similarly imperfect, one group merging gradually into the other. The fact that the boundary is not strictly defined does not impair the usefulness of the classification. An illustration from outside the domain of chemistry may help to make this point clear. If we were asked to describe the Continent of Europe, we should certainly begin by naming various countries, such as France and Germany. Everyone has a sufficiently definite idea as to what these names denote to make them useful (in fact, practically necessary) in any detailed description, whatever standpoint we adopt. Nevertheless, as soon as we attempt to establish a logical boundary between France and Germany, we find ourselves confronted with a difficulty which has baffled mankind for centuries! There is no indisputable line where French predominance logically ends and German predominance logically begins; the inhabitants of the border zone merge gradually and almost indistinguishably from one race and language to the other. It would be foolish, merely because of this fact, to deny the existence of France and of Germany as separate countries with distinct characteristics. In the same way, no one would dream of abandoning the convenient division of the year into the four seasons just because we get some winter days in spring, or *vice versa*. Bearing all this in mind, we see that the chemist is perfectly justified in using terms, such as metals and non-metals, polar compounds and non-polar compounds, as an aid in classifying the science, even although he is unable to assign every single case definitely into one class or the other.

Elements with More Than One Valence. — A final difficulty in connection with valence may be more easily disposed of. A number of the elements exhibit two (or even more) valences, according to the conditions under which combination with other elements takes place. There is, of course, no reason at all why an element which can exercise *different types* of valence should be restricted to the same valence number in all types, and a simple rule correlating positive and negative valence for such elements as do function in both ways will be presented in a later chapter (p. 489). We shall concern ourselves here only with cases where the *same type* of valence is variable, in other words where an atom of one element is found to form stable compounds with two, or even more different numbers of atoms of the same second element. This fact has already been mentioned, for it is implied in the law of multiple proportions (p. 47).

Thus, phosphorus is usually quinquivalent, and gives compounds like PCl_5, P_2O_5, PBr_5. But it can also form compounds in which it is trivalent, like P_2O_3, PCl_3. Similarly, iron forms two complete series of compounds:

Bivalent (ferrous):	$FeCl_2$,	FeO,*	$Fe(OH)_2$,	$FeSO_4$.
Trivalent (ferric):	$FeCl_3$,	Fe_2O_3,*	$Fe(OH)_3$,	$Fe_2(SO_4)_3$.

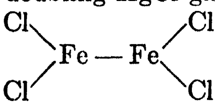
The fact that an element, under different conditions, may exhibit different valences, even of the same type, need not confuse the student as to the utility of the general conception of valence. Although it is possible for an atom of phosphorus to combine with five atoms of chlorine, this does not make it necessary that the maximum combining capacity should be exercised in all of the compounds of phosphorus. To use an analogy, the circumstance of a man having five dollars in his pocket which he is at liberty to spend does not compel him to squander the whole five dollars; he may under certain circumstances decide to save two. When an element exhibits less than its maximum valence in any given compound, it is said to be *unsaturated.* Just as the man in our illustration above still has two dollars to spend if a change of circumstances induces him to change his mind, so phosphorus in phosphorus trichloride may become *saturated* by the combination of

* FeO and Fe_2O_3 belong to the two regular series of compounds of iron. But there is the magnetic oxide, Fe_3O_4, where the valence of iron appears not to be a whole number, but 8/3 or 2⅔. In this case the chemist makes the valence regular by proving the magnetic oxide to be a compound of the other two oxides (see p. 906), and writing its formula FeO,Fe_2O_3.

each atom of phosphorus in the compound with two additional atoms of chlorine to form phosphorus pentachloride. The conditions necessary for this combination to persist will be discussed later (p. 193).

As a rule, an element passes from one form of combination to another without change of valence. But compounds of many elements, like tin or manganese, can undergo changes in the course of which the valence alters. Such changes will be discussed fully when we encounter examples of them in later chapters (see, in particular, pp. 376–80).

When the conception of valence was first evolved, it was taken for granted, quite mistakenly, that each element had only one valence. Hence, when pairs of compounds like CuCl and $CuCl_2$, or HgCl and $HgCl_2$, or $FeCl_2$ and $FeCl_3$ were considered, and it was assumed that copper was *always* bivalent, mercury bivalent, and iron trivalent, the formulæ had to be distorted to fit this assumption. Hence the formula of cuprous chloride was written, and is still often written, Cu_2Cl_2. The formulæ of the two chlorides, written graphically (p. 146) then became: Cl — Cu — Cu — Cl and Cl — Cu — Cl. In both, each atom of copper was holding (on paper), two other atoms, and was therefore bivalent (on paper). Similarly doubling HgCl gave Cl — Hg — Hg — Cl, and doubling $FeCl_2$ gave



, where the mercury appeared to be bivalent and the iron trivalent. Later, however, when elements like indium were found to have three valences, *e.g.*, InCl, $InCl_2$, and $InCl_3$, and the compounds of manganese could not be classified unless five different valences were admitted, and many other elements turned out to be multi-valent, the idea of a fixed valence for each element was given up. It is entirely contrary to the scientific method to invent or to distort facts so as to procure support for a notion which is a mere assumption, and not founded upon experiment. Yet the history of the science shows that such errors were frequently committed.

The fact is that a free element, like mercury, has no valence *actually in use,* for its atomic weight is not combined with even one equivalent of any other element. When combined, mercury shows two different valences, as in Hg_2O and HgO, HgCl and $HgCl_2$, $HgNO_3$ and $Hg(NO_3)_2$.

Nomenclature. — The names of compounds containing only two elements (the true binary compounds) end in **ide.** Such are the

oxides, as ferric ox*ide* Fe_2O_3; the carb*ides*, as aluminium carb*ide* Al_4C_3; the chlor*ides*, as sodium chlor*ide* NaCl; the sulph*ides*, as ferrous sulph*ide* FeS, etc. This applies also to compounds containing *positive* compound radicals, as ammonium chlor*ide* $(NH_4)Cl$.

When an element forms two (or more) compounds with another element, they are frequently distinguished thus: carbon *di*oxide CO_2, carbon *mono*xide CO; phosphorus *pent*oxide P_2O_5, phosphorus *tri*oxide P_2O_3.

To distinguish two compounds of the same elements, another plan is also used; ferr*ous* chloride $FeCl_2$, ferr*ic* chloride $FeCl_3$; mercur*ous* oxide Hg_2O, mercur*ic* oxide HgO. The suffix *ous* indicates that the metal is combined with the smaller proportion of the negative element, and *ic* that it is combined with the larger proportion.

The tendency — although not a universal rule — is to use the latter plan with compounds containing a metal and the former with compounds containing only non-metals.

Equivalent Weights. — In the foregoing discussion of valence, we have more than once used the word "equivalent." For example, (p. 145), it was stated that the atomic weight of aluminium is *equivalent* to three atomic weights of hydrogen, because it displaces them, and to three atomic weights of chlorine, because it combines with that number:

	$2Al$	$+$	$6HCl$	$\rightarrow$	$2AlCl_3$	$+$	$3H_2$
Weights:	2×26.97		6×36.468		2×133.35		6×1.008

Now chemists often view this from the other direction, and say that 1.008 g. of hydrogen (one atomic weight) are displaced by 8.99 g. of aluminium (one-third of the atomic weight) and that 35.46 g. of chlorine combine with just this same quantity, 8.99 g. of aluminium. When taking this view, they refer to **the weight of an element displacing one atomic weight of hydrogen,** or **combining with one atomic weight of chlorine** (or of any other univalent element) as the **equivalent weight of that element.** The equivalent weight of aluminium is therefore 8.99.

Thus **the valence of an element** may be defined as **the number of equivalent weights contained in its atomic weight.** Arithmetically it is the integer by which the equivalent weight was multiplied in forming the atomic weight.

It will be seen that the equivalent weight can always be found by a quantitative experiment. It is also evident that the equivalent weight of an element is the atomic weight divided by the valence. The conception of equivalent weights finds important application in several connections in chemistry (see Normal Solutions and Faraday's Law).

The Basis of Equivalent Weights, Oxygen = 8. — It has been shown above that the equivalent weight of any element is its atomic weight divided by its valence. Now all of our atomic weights are represented on the basis oxygen = 16, and in all of the common compounds of oxygen this element is bivalent. Consequently equivalent weights are based upon the fundamental standard: oxygen = 8.

Historically, in the earlier development of the atomic theory, equivalent weights and atomic weights were frequently confused. When chemists found, for example, that in the most familiar compound of hydrogen and oxygen (water) the proportions by weight were one of hydrogen to eight of oxygen, they naturally assumed that these proportions expressed the relative atomic weights of the two elements. Similarly, when methane, the simplest compound of carbon and hydrogen, was analyzed and found to contain 3 parts by weight of carbon to 1 of hydrogen, the value of the atomic weight of carbon was assumed to be 3, on the basis oxygen = 8. And when, finally, analysis of carbonic acid gas (carbon dioxide), the most common compound of carbon and oxygen, gave a ratio of 3 parts by weight of carbon to 8 of oxygen, this assumption seemed to be completely justified.

It was not long, however, before further experiments showed that the idea that the most familiar compound of two elements always contained those elements in equal atomic quantities could not be logically sustained, and by degrees the true atomic weights were substituted for the original equivalents. The determining factor in convincing chemists of the necessity of such substitutions was the acceptance of Avogadro's hypothesis (p. 181), which removed all excuse for confusion between the atomic and the equivalent weights of elements such as oxygen and carbon, as we shall see in Chapter XI. Although equivalent weights are of considerable *practical* interest, yet the fundamental importance of atomic weights in the development of chemical theory is so preponderant a factor that the abandonment of the old equivalent weight basis (oxygen = 8) for

the modern atomic weight basis (oxygen = 16) in formulæ and equations is now universal.

A Suggestion. — Having just discussed the conception of valence, we have now considered most of the more important general laws of chemical composition. At this point the reader should pause to take breath and *review thoroughly the subjects of the first nine chapters.* The understanding of the fundamental principles which this retrospect will give will greatly lighten the task of understanding the new and more complex substances we shall have to consider, and the new kinds of reactions and new conceptions we shall encounter, in the chapters immediately following.

Exercises. — 1. Mark the valences in the formulæ: $InCl_3$, V_2O_5, OsO_4, $PtCl_4$.

2. Mark the valences of the radicals in the formulæ: $Zn(SeO_4)$, $Al_2(TeO_4)_3$, $H_3(AsO_4)$, $H(SbO_3)$.

3. If 26 g. of chromium displace 1 g. of hydrogen from hydrochloric acid, what is the valence of chromium in this displacement (see Table of Atomic Weights)?

4. Correct the following formulæ: $CaNO_3$, $CaPO_4$, $Al(PO_4)_2$, LiO, PbF, $Bi(NO_3)_2$.

5. One gram of a quadrivalent element unites with 0.27 g. of oxygen. What is the atomic weight of the element?

6. What are the valences of the elements in the following: LiH, NH_3, SeH_2, BN?

7. What are the valences of the metals and radicals in the following: HNO_3, $Pb(NO_3)_2$, $Ce(SO_4)_2$, KCl, $KMnO_4$ (potassium permanganate)? Name all the substances in 6 and 7.

8. What is wrong with the statement: The valence of oxygen is two because the molecular formula is O_2?

9. Silver oxide contains 93.10 per cent by weight of silver. Calculate the equivalent weight of the metal. What is its valence?

10. The atomic weight of tin is 118.7; the element is quadrivalent. What is its equivalent weight? What is the formula of its compound with oxygen? What is the percentage composition of the compound?

11. Osmium, a metal of the platinum group (p. 815), forms an oxide OsO_4. What is the valence of osmium in this compound? The metal also forms a fluoride OsF_8. What is the valence of fluorine?

12. When 1 g. of magnesium is burnt in oxygen, 1.658 g. of magnesium oxide are formed. What is the equivalent weight of magnesium?

13. The equivalent weight of indium was found by experiment to be 38.3. Its specific heat is 0.0577. What is its atomic weight? What is its valence?

14. 0.279 g. of a metal, when treated with dilute sulphuric acid, displaced 118.9 c.c. of hydrogen at 15° and 756 mm. Find the equivalent of the metal.

15. Antimony forms three compounds with oxygen, with the following percentage compositions: (*a*) antimony 83.35, oxygen 16.65; (*b*) antimony 78.98,

oxygen 21.02; (*c*) antimony 75.03, oxygen 24.97. The specific heat of antimony is 0.0508. What is its atomic weight and what is its valence in each of the three oxides?

READING REFERENCE

Kendall; At Home among the Atoms, Chapter X.

CHAPTER X

WATER

This is the most important, as well as the most plentiful, of all compound substances. The human body is saturated with it, and water to make up for evaporation, as well as to aid in digestion, is a most necessary part of our food. The ocean covers about three-fourths of the surface of the earth, and the "dry" land would be uninhabitable if it were really dry. The air always contains more or less water vapor.

All statements of physical and chemical properties in this chapter refer, it may be noted, to ordinary water. It has been discovered recently that this contains a very small fraction of **heavy water**, the hydrogen atoms of which have a mass twice that of ordinary hydrogen, with properties that are significantly different (compare p. 43). This highly important development will be discussed in detail in a later chapter (pp. 482–3).

Measurement of the Composition by Weight.—An arrangement by which the proportion by weight of hydrogen and oxygen in water can be roughly determined is shown in Fig. 74. The bulb *A* contains cupric oxide, which is heated. Hydrogen from a generator or cylinder enters on the left and reduces the oxide, forming copper and water:

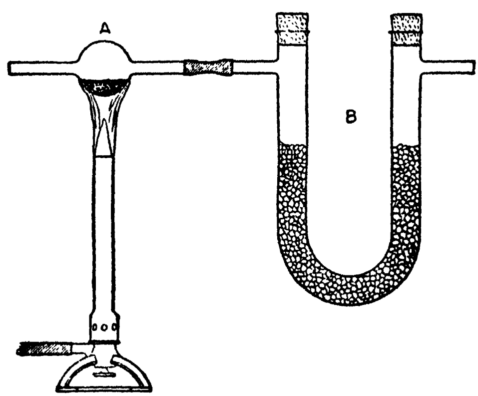


FIG 74. Composition of Water by Weight.

$$H_2 + CuO \rightarrow H_2O + Cu.$$

The water is carried as vapor by the excess of hydrogen and passes into the **U**-tube *B*. This tube contains calcium chloride, a substance

which absorbs water greedily and is used therefore for drying gases. Here the water is all caught, while the hydrogen passes on. The tubes A and B with their contents are weighed just before, and again just after, the experiment. The loss of weight in A is the weight of the oxygen. The gain in weight in B is the water. The difference between these numbers is the hydrogen. It is found that the weights of hydrogen and oxygen thus ascertained, when all precautions are taken to eliminate casual experimental errors, stand in a ratio of 1 (Hydrogen) : 7.94 (Oxygen) or, using the standard value oxygen = 8 to express our results as equivalent weights, in the ratio of 1.008 : 8.

From 1842 until 1888, the accepted value of this proportion was that of the French chemist, Dumas. His experiments gave the ratio of hydrogen to oxygen 2 : 15.96, or 2 × 1.0025 : 16. Cooke and Richards (1888) obtained a figure for the oxygen appreciably smaller than this, namely 2 : 15.90, or 2 × 1.0063 : 16, and Lord Rayleigh (1889) 2 : 15.926. W. A. Noyes (1889–1907) made many determinations and, finally, from twenty-four measurements obtained the ratio 2 : 15.875, or 2 × 1.0079 : 16.

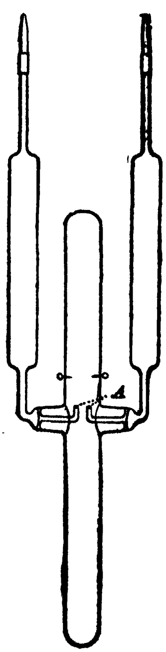


FIG. 75. Morley's Apparatus.

The investigation (lasting twelve years) which finally settled this question was that of Edward Morley. The most striking of his experiments consisted in a series of syntheses of water, in which he weighed the hydrogen as well as the oxygen, and afterwards weighed the water produced from them. The hydrogen was confined by adsorption in palladium (p. 139), and could thus be contained in large quantity in a small, elongated bulb. During the progress of the experiment it was driven out by a suitable heating arrangement. The oxygen was contained in large globes holding 15–20 liters. The losses in weight of the palladium tube and of the globes gave the hydrogen and oxygen consumed. The manipulator in which the gases were combined and the water collected is represented in Fig. 75. The gases entered through two small tubes marked A. Just above them, between two platinum wires, a discharge of electricity started the union and when necessary maintained it. The vessel was first filled by admitting oxygen, and the hydrogen was burned at the mouth of the tube from which it issued. This part of the apparatus was immersed in a vessel of water with transparent walls through which the union could be watched, and the steam formed was condensed and collected in the bottom of the vessel. The vacuum thus produced enabled the oxygen continually to flow into the manipulator from the globes. In this way forty-two liters of hydrogen and twenty-one liters of oxygen could be combined in about an hour and a half.

At the end of the experiment this part of the apparatus was disconnected and

placed in a freezing mixture which converted the water into ice and practically condensed the whole of its vapor. The uncombined gas in the apparatus was withdrawn and its nature and quantity determined. The increase in weight of the manipulator gave the quantity of water formed. The success of each experiment could be tested by comparing the sum of the weights of oxygen and hydrogen with that of the water obtained from them. The manipulation was so skilful, and the various corrections used were so adequate, that this difference was almost negligible. The ratio of hydrogen to oxygen in water in this series of experiments was 2 : 15.879 (or 2 × 1.0077 : 16), a result which agreed with other methods of determining the same ratio which Morley used. It agrees also with the average of the numbers obtained by later observers.

Measurement of the Composition by Volume. — The proportions by volume in which hydrogen and oxygen combine may be shown by introducing the two gases into a tube called a **eudiometer,** filled with mercury and inverted in a cylinder of mercury (Fig. 76). The volumes, at atmospheric pressure, are read by lowering the tube, after the introduction of each gas, until the levels of the mercury inside and outside are alike. A spark from an induction coil passed between the platinum wires inserted at the top of the tube causes the union of the gases. The water condenses to a slight dew and the volume of the single gas which remains is measured. Thus, if 19.5 c.c. of oxygen and 20 c.c. of hydrogen are taken, the corrected volume of gas remaining is 9.5 c.c. and this gas is afterwards found to be oxygen. The volumes consumed were therefore 19.5 — 9.5 = 10 c.c. of oxygen and 20 c.c. of hydrogen. The ratio by volume is therefore 2 Hydrogen : 1 Oxygen. If these exact proportions are used, the mercury fills the tube completely after the explosion, but is apt to break it by striking the top violently.

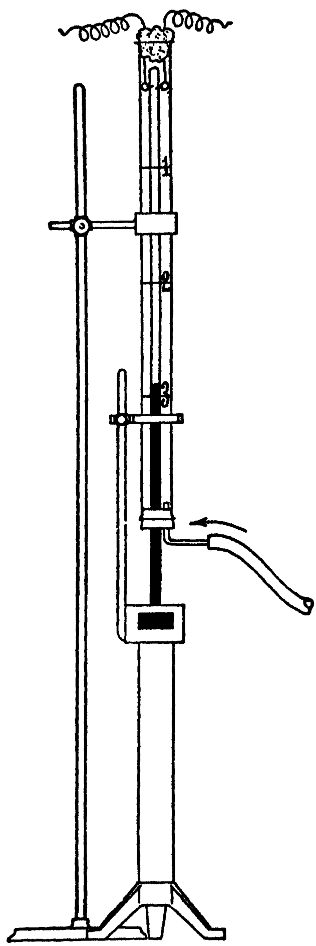


FIG. 76. Eudiometer (Composition of Water by Volume).

Combining the most reliable work on the densities of hydrogen and oxygen (p. 117) with the results of Morley on the combining proportions by weight, we arrive at the ratio 2.0027 volumes of hydrogen to 1 volume of oxygen as the most probable precise value for the combining proportions by volume at 0° and 760 mm. Experiments at other temperatures and pressures indicate that the small deviation from the simple ratio 2 : 1 is not fundamental, but depends upon the fact that the two gases are not absolutely perfect (see p. 125). When correction is made for their respective non-idealities in behavior, the final volume ratio attained is, within the limits of experimental error, *exactly* 2 : 1.

When the above experiment is carried out at 100°, in order that the product, water, may be gaseous also, it is found that the three volumes of the constituents give almost exactly two volumes of steam. For example, 15 c.c. of hydrogen and 7.5 c.c. of oxygen give 15 c.c. of steam. Of course the hydrogen, oxygen, and steam must be measured at the same pressure, and the temperature must remain constant (100°) during the experiment. Proper manipulation secures the former, and a jacket filled with steam (Fig. 76) the latter condition. Strips of paper, 1, 2, and 3, are pasted on the jacket in such a way that equal lengths of the eudiometer are laid off. The three divisions having been filled with a mixture of hydrogen and oxygen in the proper proportions, the gas, after the explosion, shrinks so as to occupy, at the same pressure, only two of them. That is to say:

$$1 \text{ Vol. Oxygen} + 2 \text{ Vols. Hydrogen} \rightarrow 2 \text{ Vols. Steam.}$$

Gay-Lussac's Law of Combining Volumes. — When other chemical actions between gases are studied in the same way, it is found that, in every case, **the volumes of the gases used and produced in a chemical change can always be represented by the ratio of small whole numbers.** This fact is exceedingly interesting. It was first discovered by Gay-Lussac in 1808. There is no such relation amongst the combining proportions by *weight*, which can be expressed only by the employment of entirely unrelated large numbers (see p. 48), each applying to one particular element only, so that this evidence of the existence of a simple and general rule in regard to combining proportions is the first we have encountered and is very welcome. The use made of it by the chemist will be developed in the next chapter.

Physical Properties of Water. — A deep layer of water has a blue or greenish-blue color. At a pressure of 760 mm., water exists as a liquid between 0° and 100°. Below 0° it becomes solid, above 100° a gas. Of all chemical substances it is the one which we use most, so that its physical properties, discussed below, should be studied attentively. Then, too, what is said of water is in general true of all other liquids, from which it differs only in details.

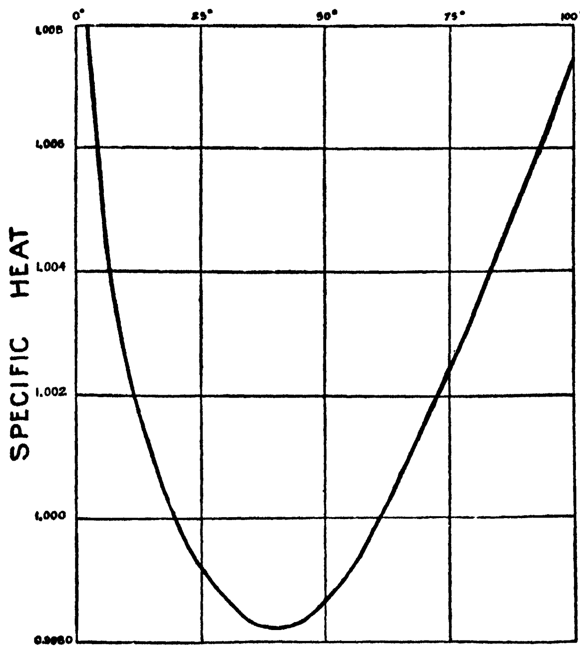


FIG. 77. Variation in Specific Heat of Water with Temperature.

The average quantity of heat required to raise one gram of water one degree in temperature, between 0° and 100°, is called **a calorie,** the unit quantity of heat. The specific heat of any substance being the quantity of heat required to raise the temperature of one gram of the substance one degree, the average specific heat of water throughout this temperature range is 1. The values at 0° and 100° are slightly higher than those in the middle of the range, but the variation from unity is never so great as 1 per cent (see Fig. 77). The values for all other common materials are much smaller: *e.g.*,

limestone 0.2; notice, however, that hydrogen (p. 138) has a specific heat of 3.4. Thus the temperature of large masses of water, such as lakes and seas, changes more slowly, and within a smaller range, than that of the rocks and soil composing the land. The more constant temperature of the water tends to regulate that of the air, and hence the climate of an island is less variable from season to season than is that of a continent.

The weight of a cubic centimeter of water at 4° is 1 gram. At this temperature water possesses its *maximum density;* not only does it expand when heated, but it also expands slightly when cooled (see Fig. 78). Thus a kilogram of water at 0° occupies 1000.159 c.c., or 0.132 c.c. more than at 4° (see exercise 18, p. 19). The volume of a kilogram of water at 100° is 1043.2 c.c. Nearly every substance contracts regularly on cooling, and this expansion of water between 4° and 0° is very unusual.

Perfectly pure water is an *exceedingly* poor conductor of electricity. Ordinary tap-water owes its small capacity for conducting almost entirely to traces of impurities (see p. 171). Many substances, however, when dissolved in water, give solutions which are extremely good conductors. Sulphuric and hydrochloric acids are examples which we have already encountered (p. 134). This is a point which will be taken up in detail later.

Ice. — The raising or lowering of the temperature of a gram of water through one degree involves, we have seen above, the addition or removal of approximately one calorie of heat. The conversion, however, of a gram of water at 0° to a gram of ice at 0° requires the removal of 80 calories. The mere melting of a gram of ice causes an absorption of heat to the same amount, called the **heat of fusion of ice.** At 0° a mixture of ice and water will remain in unchanged proportions indefinitely. Any cause which tends *permanently* to lower or raise the temperature by a fraction of a degree, however, will bring about the disappearance of the water or of the ice, respectively. This *equilibrium* temperature is called the **melting-** or the **freezing-point.**

Water can be cooled below 0° (supercooled) without beginning to freeze, unless it is stirred, or "inoculated" by the addition of a piece of ice. Hence, the freezing-point is not defined as the point at which ice begins to form, for that point varies, and is always below 0°, but as the temperature of a well-stirred *mixture* of ice and water.

Water expands very considerably on solidification, a kilogram

of ice at 0° occupying 1090.83 c.c., or 90.7 c.c. more than an equal weight of water at the same temperature. This is again very unusual, since nearly all substances contract on changing from the liquid to the solid state. It plays a very important part, however, in the economy of nature. If ice were heavier than water, it would

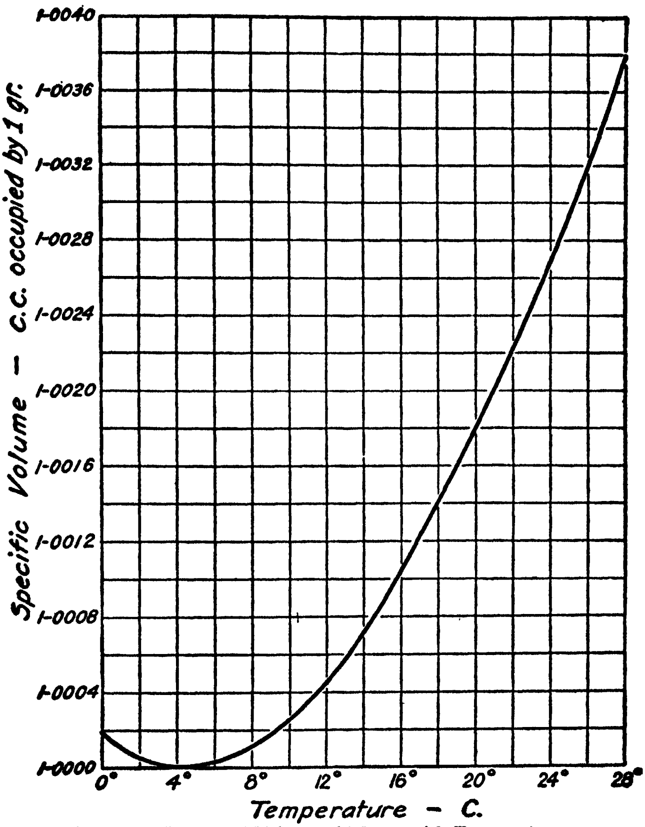


FIG. 78. Change of Volume of Water with Temperature.

sink to the bottom as soon as formed, and rivers and lakes would soon become entirely frozen.

The States of Matter: Transition Points. — Most substances are known in three different states of aggregation, a solid (or crystalline), a liquid, and a gaseous form. There is no magic about the number, three, however. Thus, sulphur has a vapor state, two liquid states, and several different crystalline forms. There are no

fewer than five forms of ice, different in *physical* but identical in *chemical* properties.

All transitions from one state to another take place at some definite temperature (when the pressure is fixed). Such temperatures, when referring to the change from the solid to the liquid, and from the liquid to the gaseous state, are called the melting-point (or freezing-point) and the boiling-point, respectively, or in general, are known as **transition points.** Properties of this kind are much used in chemistry for keeping other bodies or systems at a constant temperature during measurement or observation. A mixture of ice and

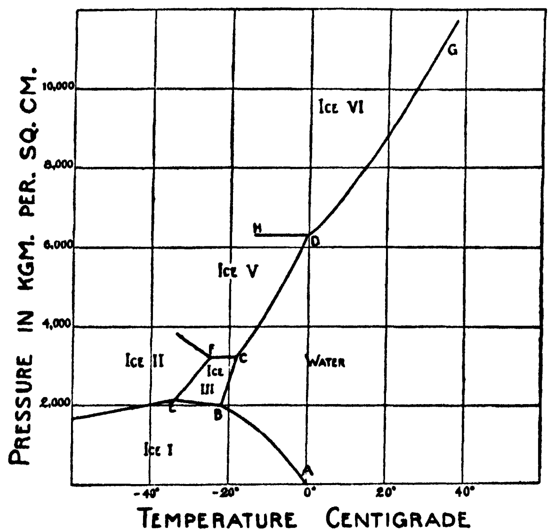


Fig. 79. Ice-Water Equilibrium at High Pressures.

water surrounding a body, when kept in constant agitation, will automatically maintain the body at a fixed temperature (0°) so long as both components hold out.

When we wish to transform a substance from one state to another, we change its *conditions* (see p. 38). Thus under atmospheric pressure water is converted to ice by reducing the temperature below 0°, and to steam by raising it above 100°. Under a pressure of 100 atmospheres, however, water freezes at —1°, and boils only at 330°. With still higher pressures, the change in the freezing-point is much more marked. Thus under 2000 atmospheres pressure water does not freeze above —20°. If the pressure is increased further, different crystalline forms of ice make their appearance

(see Fig. 79), and the freezing-point rises again until under 20,000 atmospheres water is found to freeze at $+ 78°$!

Steam. — At atmospheric pressure, water passes into steam ("boils") rapidly at 100°, but at lower temperatures, and even when frozen, it does the same thing more slowly. It changes into steam, however, only when the necessary supply of heat is forthcoming. One gram of water at 100°, in turning into a gram of steam at 100°, takes up 540 calories. This is called its **heat of vaporization.** Steam, in fact, contains much more available energy than an equal weight of water at the same temperature, just as water, in turn, contains more energy than ice. At 100° steam occupies nearly 1600 times the volume of an equal weight of water.

Steam is a colorless, invisible gas. The visible cloud of fog, seen when steam escapes into cold air, is composed of minute drops of water, formed by condensation, and visible because they have *surfaces* and reflect light.

The temperature of 100° is, like the melting-point of ice, an important transition point. It is less exactly recoverable by simply keeping a vessel full of water in ebullition, however, because the natural, and often considerable, variations in the pressure of the atmosphere affect it more markedly than they do the melting-point of ice. Near to 100°, the boiling-point rises or falls about 0.037° for 1 mm. change in pressure. On the top of Mont Blanc water boils at 84°. The melting-point of ice is lowered only 0.0075° by an increase in pressure from 760 mm. to 2 atmospheres (1520 mm.).

Aqueous Tension and Vapor Pressure. — The transition of water from the liquid to the gaseous state deserves somewhat more extended study.

The most significant fact about this transition is that, *when excess of the liquid is present*, the pressure of the vapor above the liquid quickly reaches a definite maximum value for each temperature. In the absence of excess of the water, *less* than this maximum pressure may exist. *More* than the maximum pressure proper to a given temperature, if produced by compression, cannot be maintained, however, for a part of the vapor condenses to the liquid state. The magnitude of this maximum vapor pressure, at a given temperature, depends on the tendency of the particular liquid to pass over into vapor. This maximum vapor pressure is held, therefore, to represent the **vapor tension of the liquid,** at the given temperature, and this is a specific property of the substance.

The vapor tension of water may very easily be measured by allowing a few drops to ascend into a barometric vacuum (Fig. 80). The tube on the left shows the original height of the mercury. The tube on the right shows the result of admitting the water. The pressure of the atmosphere being the same for both, the smaller height of mercury which now suffices to counterbalance it shows that something, which can be nothing but the water vapor, is pressing on the surface of the mercury, and makes up the rest of the total stress needed. The difference in the height of the two columns gives the value of the pressure of the water vapor. With a minimum excess of water, the value is that of the vapor tension, called, in the case of water, the **aqueous tension.**

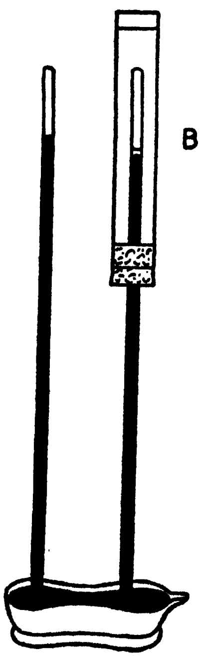


FIG. 80. Measurement of Aqueous Tension.

The jacket B surrounding the tube on the right enables us, by adding ice or warm water, to maintain any temperature between 0° and 100°. Even at the freezing-point, when ice is used outside, and a piece of it is introduced into the vacuum, the vapor it gives off quickly reaches a pressure of 4.5 mm. The vapor pressure of the ice (or of liquid water) at 0° takes the place of 4.5 mm. of mercury in balancing the atmospheric pressure, and so the mercury column falls by this amount. Similarly, water at 10° causes a fall of 9.1 mm. and at 20° of 17.4 mm., so that these represent the mercury-height values of the aqueous tension at these temperatures. The *quantity* of water used makes no difference, so long as *a little* more is present than is required to saturate (see below) the available space with vapor. With ether, instead of water, at 10°, the fall is 28.7 mm.

With water at higher temperatures the fall of the mercury column becomes much greater (see Fig. 81). At 50° it is 92 mm., at 70° it is 233.3 mm., at 90° it is 525.5 mm., and at 100° it is 760 mm., or one atmosphere. At 121° the aqueous tension is two atmospheres, at 180° it is ten atmospheres (see Appendix IV).

When water at a certain temperature has given the full amount of water vapor to the space above it that its aqueous tension permits, we say that the space is **saturated** with vapor. That con-

centration of vapor which constitutes saturation varies with the temperature of the water and depends, therefore, solely on the power of the water to give off vapor. It has nothing to do with the size of the space, and is even independent of other gases the space may already contain. Thus, if a little air is first placed above the dry mercury (Fig. 80) causing it to fall, the *additional* depression produced by adding water is the same as if the air had been absent (Dalton's law of partial pressures, p. 116).

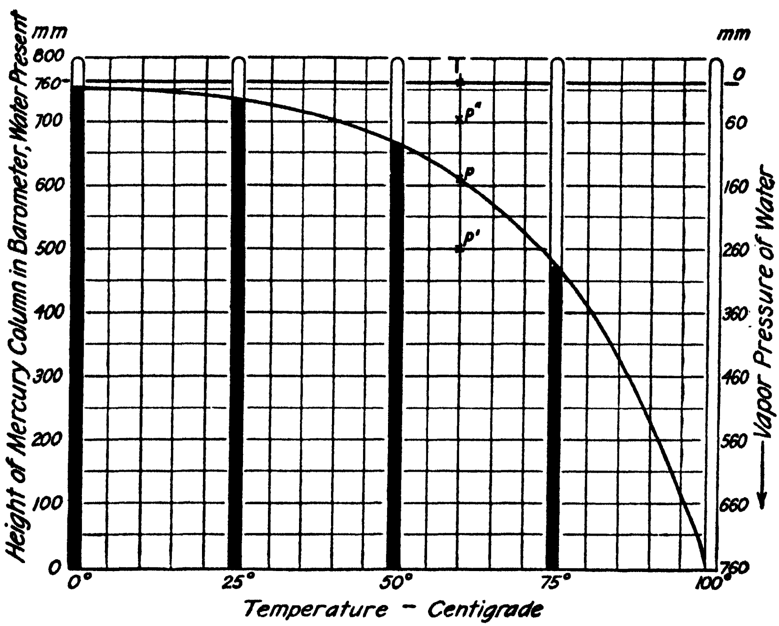


FIG. 81. Vapor Pressure Curve of Water from 0° to 100° C.
The insertion of the barometer tubes emphasizes the physical significance of the curve. To obtain vapor pressure values, use the scale at the right of the diagram and read *downwards*.

The Properties of Liquids and the Kinetic-molecular Hypothesis. — The fact that even great pressures produce little diminution in the volume of a liquid shows that the free space, so predominant in gases, is relatively unimportant in liquids. This is only natural in view of the smaller volume occupied by substances in the liquid state. Thus we have seen (p. 165) that steam at 100° occupies nearly 1600 times the volume of an equal weight of water. To reduce a given sample of water to four-fifths its original volume requires, not raising the pressure to five-fourths its initial value as

in the case of a gas, but increasing it from 1 to 10,000 atmospheres. Evidently the molecules are already very closely packed.

This close packing of the molecules causes *cohesion* to be much more pronounced in liquids than in gases. A small amount of liquid, when poured into a vessel, does not fill the whole of the available space, but forms coherent drops, the curvature of the surface of which indicates that tremendous forces are existent, pulling the outside molecules toward the interior of the liquid. Nevertheless, molecules do escape outwards from a liquid surface to form vapor, and their escape is more easily effected the higher the temperature (see pp. 166–7). We must therefore conclude that the molecules of a liquid are still in rapid motion. Similarly, when liquids which are capable of mixing (*e.g.*, alcohol and water) are placed in separate layers in the same vessel, they do mix, slowly, by *diffusion*. The rate of dispersion of the molecules, although much impeded by their close packing, has not been annihilated.

A liquid still possesses, therefore, in a modified degree, many of the properties exhibited by a gas. The average velocity of the molecules increases with temperature, while the cohesive forces between them diminish. For any particular substance, the differences between the behavior of the liquid and the gaseous states grow less and less as the temperature is raised, until finally at the *critical temperature* (see p. 124) the two states become absolutely identical.

Liquid Crystals.—Liquids at temperatures near the freezing-point also possess, in a modified degree, certain of the properties exhibited by solids. X-ray analysis shows, for example, that sub-microscopic crystal nuclei are present in larger and larger quantities in a liquid as the temperature is lowered, although it is only when the freezing-point is reached that these nuclei are capable of coalescing to form a continuous space lattice. The formation of significant quantities of incipient crystals in water just above its freezing-point is indicated by the expansion in volume which occurs between 4° and 0° (p. 162). In highly supercooled liquids, such as glass (p. 62), coalescence may be prevented by the high viscosity of the medium.

When most solids are heated, the forces holding the units of the space lattice in position break down simultaneously in all three planes, so that the transition from crystal to liquid is apparently abrupt. Instances are known, however, where the forces holding the units together are much weaker in one plane than in others, and here intermediate stages are observable. Many organic substances, for example, resemble graphite (see Fig. 162, p. 560) in building up crystal structures consisting of compact sheets relatively loosely held together. Others, again, resemble soap (see p. 643), and consist of long chains or threads, only loosely linked one with another. With both types we may obtain the peculiar phenomenon of **liquid crystals.**

Thus *para-azoxyanisole* $C_{14}H_{14}O_3N_2$ "melts" sharply at 118° to give a turbid

liquid, which still exhibits crystalline properties (*e.g.*, double refraction, p. 63). At 136° the milky liquid suddenly becomes clear and loses all crystalline characteristics. The reverse series of changes occurs on cooling.

Molecular Relations of Liquid and Vapor. — When the water was introduced above the barometric column, the vapor, or gaseous water, could have resulted only from the spontaneous motion of the molecules in the liquid. Some of the molecules, moving from the surface, went off into the space above the water and became gaseous. To be consistent, we must also conclude that the vapor above the water is not composed of the *same* set of molecules one minute as it was during the preceding minute. Their motions must cause many of them to plunge into the liquid, while others emerge and take their places. When the water is first introduced, there are no molecules of vapor in the space at all, so that emission from the water predominates. The pressure of the vapor increases as the concentration of the molecules of vapor becomes greater, hence the mercury column falls steadily. At the same time the number of gaseous molecules plunging into the water per second must increase in proportion to the degree to which they are crowded in the vapor. The rate at which molecules return to the water surface thus begins at zero, and increases steadily; the rate at which molecules leave the surface maintains a constant value. Hence the rate at which vapor molecules enter the water must eventually equal that at which other water molecules leave the liquid. At this point, occasion for visible change ceases and the mercury comes to rest. We are bound to think, however, of the exchange as still going on, since nothing has occurred to stop it. The condition is not one of rest but of rapid and equal exchange. Such, described in terms of molecules, is that state of affairs which is characteristic of a condition of **equilibrium.** The condition is dynamic, and not static.

Equilibrium. — This term is used so often in chemistry, and is used in so unfamiliar a sense, that the reader should consider attentively what it implies. Three things are characteristic of a state of equilibrium.

1. There are **always two opposing tendencies** which, when equilibrium is reached, balance each other. In the foregoing instance, one of these is the hail of molecules leaving the liquid, which is constant throughout the experiment. It represents the **vapor tension of the liquid.** The other is the hail of returning molecules,

which, at first, increases steadily as the concentration of the vapor becomes greater. This is the **vapor pressure of the vapor.** These have the effect of opposing pressures and, when the latter becomes equal to the former, *equilibrium* is established. In all the cases of equilibrium which will be encountered, we shall symbolize the two opposing tendencies by *two* arrows, thus:

$$\text{Water (liquid)} \rightleftarrows \text{Water (vapor)}.$$

2. Although their effects thus neutralize each other **at equilibrium, both tendencies are still in full operation.** In the case in point, the opposing hails of molecules are still at work, but neither can effect any visible change in the system. Equilibrium is a state, not of rest, but of balanced activities.

3. (This is the *chief* mark of equilibrium.) **A slight change in the conditions produces,** never a great or sharp change, but always, and instantly, **a corresponding small change in the state of the system.** The change in the conditions accomplishes this by **favoring** or **disfavoring one of the two opposing tendencies.** Thus, for example, when the *temperature* of a liquid *is raised,* the motion of its molecules is increased, the rate at which they leave its surface becomes greater, the vapor tension increases and, hence, a greater concentration of vapor can be maintained. The system, therefore, quickly reaches a new state of equilibrium in which a higher vapor pressure exists.

In the preceding illustration, the evaporating tendency was *favored* by a rise in temperature. As an example of a change in conditions *disfavoring* one tendency, take the case where the liquid is placed in an *open,* shallow vessel. Here the condensing tendency is markedly discouraged, for there is little chance of return of the emitted molecules. Hence complete evaporation finally takes place. Elevation of the temperature hastens the process. A draft insures the diffusion of the vapor away from the surface of the liquid, and has therefore the same effect. These two methods of assisting the displacement of an equilibrium, and particularly the second, in which the opposed process is weakened and the forward process triumphs solely on this account, should be noted carefully. They are applied with surprising effectiveness in the explanation of chemical phenomena (see Chaps. XVI and XIX).

Water as a Solvent.—The physical property of water most frequently made use of in chemical work is its remarkable power of *dissolving* many other substances. This subject is so important and extensive that we shall presently devote a complete chapter to some of its simpler and more familiar aspects.

Natural Waters. — The water found in nature varies greatly in the amount of foreign material which it contains. Sea-water holds about 3.6 per cent of solid matter in solution, while rain-water is the purest natural water. Even rain-water contains foreign matter, however. When we heat it, bubbles of gas form on the sides of the vessel, showing that oxygen, nitrogen, and carbon dioxide from the air have been dissolved by the water as it fell. On evaporating a considerable mass of such water, we find that, aside from casual dust, crystals of definite chemical substances, such as ammonium nitrate, may be recognized in the residue. River and well waters often contain calcium sulphate, calcium bicarbonate, and compounds of magnesium in solution, which act chemically upon soap (p. 640), and such waters are described as **hard.** Sometimes they contain compounds of iron, and sometimes they are effervescent and give off carbon dioxide. These are called mineral waters. All of the dissolved substances are obtained by the water in its progress over or under the surface of the ground.

Water which is to be used for domestic purposes is examined, not only to ascertain the amount of the ingredients which produce hardness, but also with reference to the proportion of organic matter which it may hold in suspension. This usually gains access to the water by admixture of sewage (p. 97). It is not the organic matter itself which is deleterious, but the bacteria of putrefaction and disease which are likely to accompany it. Cholera and typhoid fever are often spread by the drinking of water into which sewage, infected by patients suffering from these diseases, has been allowed to enter. If the water contains clay in suspension, the bacteria are largely attached to the particles of clay, which are sufficiently large to render the water turbid, but organic matter and bacteria may be present in water which looks perfectly clear. Inoculation of culture media with the water can alone show whether or not bacteria are present.

The foreign materials which water may contain are divisible into two kinds — **dissolved** matter and **suspended** matter. No natural water is entirely free from either of these varieties of impurity.

Purification from Suspended Matter and Bacteria. — The suspended impurities may be removed by filtration. On a large scale, beds of gravel are employed, but this treatment will not remove all bacteria. In many cases small amounts of alum, or alum and lime, or ferrous sulphate (copperas) and lime, are added. These produce slimy precipitates which assist in the elimination of fine,

suspended organic and inorganic matter, including practically all bacteria. This is called the **coagulation treatment** (p. 775). The whole suspended matter is then allowed to settle, which it does very quickly, in large reservoirs. The remaining organisms may be destroyed by adding a little bleaching powder (p. 375), or chlorine-water (p. 245), before the water is distributed.

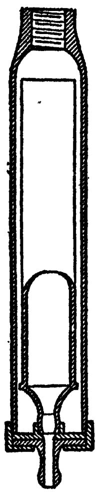


FIG. 82. Pasteur Filter.

In the household, the **Pasteur filter** is the most compact and efficient appliance. The water enters at the top (Fig. 82) and is forced inwards by its own pressure through the pores of a cylinder of unglazed porcelain. The cylinder must be taken out, and its exterior cleaned daily with a brush, to remove the mud and organisms which collect on its outer surface. If this is not done, the organisms multiply and soon the filter pollutes the water instead of purifying it.

Most organisms can be killed by boiling unfiltered water for 10 or 15 minutes, although a second boiling is needed in some cases.

Purification from Dissolved Matter. — Filtration does not remove dissolved matter, and therefore does not soften hard water. For this latter purpose, washing powders are used in the laundry (see p. 732).

Pure water for chemical purposes is prepared by **distillation** and, in fact, liquids other than water are usually purified by the same process (Fig. 11). Dissolved solids remain in the flask (or boiler). The steam is condensed by cold water circulating in the jacket of the condenser. Freshly distilled water contains only gases dissolved from the air. Such water, however, quickly dissolves traces of glass or porcelain, so that the purest water is obtained by using quartz or platinum for the condenser tube and receiving vessel. Tin is the best of the less expensive materials.

That glass dissolves in water is easily shown by shaking some pulverized glass with distilled water for a few seconds and adding a drop of phenolphthalein solution (see Indicators). The alkaline reaction of the dissolved sodium silicate gives rise to a strong pink color.

Chemical Properties of Water. — Water is so very frequently used in chemical experiments in which it is a mere mechanical ad-

junct, that the beginner has difficulty in distinguishing the cases in which it has itself taken part in the chemical interaction. The rather limited list of kinds of chemical activity it can show should therefore receive careful notice:

1. Water is a relatively stable substance.
2. It combines with many oxides, forming bases or acids.
3. It acts on certain metals, with the liberation of hydrogen and the formation of hydroxides (at low temperatures) or oxides (at high temperatures). This point has already been discussed under *displacement* in a preceding chapter. Some of the common non-metals (*e.g.*, carbon) also react with water at high temperatures, under conditions that will be described later (see p. 569).
4. It combines with many substances, chiefly salts, forming hydrates.
5. It interacts with some substances in a way described as hydrolysis. This property will not be discussed until a characteristic example is encountered (p. 231).

Water a Stable Compound: Dissociation. — In the case of a *compound*, the first chemical property to be noted is always whether the substance is relatively **stable** or **unstable** (see p. 99). Usually, the specification is in terms of the temperature required to produce noticeable decomposition. Thus, potassium chlorate gives off oxygen at a low red heat. Now, water vapor, when heated very strongly, is partially decomposed into hydrogen and oxygen,* yet at 2000° and 1 atm. pressure the maximum decomposition observable reaches only 2 per cent, and reunion occurs as the temperature is lowered. Two arrows in the equation indicate that the action may proceed in either direction — is **reversible:**

$$2H_2O \rightleftarrows 2H_2 + O_2.$$

A decomposition which increases when the temperature (or pressure) is shifted in one direction, and reverses itself by recombination of the constituents when the temperature (or pressure) is displaced in the other direction, is called **dissociation** (compare barium peroxide, p. 90). The decomposition of potassium chlorate (p. 91) is *not* a dissociation, because it is not reversible in practice: oxygen gas will not, under any known circumstances, unite directly with potassium chloride (see, however, p. 267).

* At very high temperatures the decomposition into hydrogen and the hydroxyl radical OH also becomes noticeable.

Union of Water with Oxides. — 1. Sodium oxide Na_2O unites violently with water to form sodium hydroxide:

$$Na_2O + H_2O \rightarrow 2NaOH.$$

The slaking of quicklime is a more familiar action of the same kind:

$$CaO + H_2O \rightarrow Ca(OH)_2.$$

The aqueous solutions of these two products have a soapy feeling, turn red litmus (a vegetable extract) blue, and possess other properties which, as we shall see later, are characteristic of a class of substances called alkalies or **bases.** Very many hydroxides, which are of the same nature, for example, ferric hydroxide $Fe(OH)_3$ and tin hydroxide $Sn(OH)_2$, are formed so slowly by direct union of the oxide and water that they are always prepared in other ways. The oxides which, with water, form bases are called **basic oxides.**

2. Some oxides, although they unite with water, give **acids,** which are products of an entirely different character (see p. 131). Phosphorus pentoxide P_2O_5 (p. 95), sulphur dioxide SO_2 (p. 95), and sulphur trioxide SO_3 (p. 419), are of this class and yield phosphoric acid, sulphurous acid and sulphuric acid, respectively:

$$P_2O_5 + 3H_2O \rightarrow 2H_3PO_4.$$
$$SO_2 + H_2O \rightarrow H_2SO_3.$$
$$SO_3 + H_2O \rightarrow H_2SO_4.$$

In consequence of their relation to the acid, differing from it in *not* containing the elements of water, these oxides are often called the **anhydrides** (Greek, lacking water) of their respective acids. They are also called **acidic oxides.**

These two classes of final products are so different that we make the distinction the basis of classification of the elements present in the original oxides. The elements, like sodium and iron, whose oxides give bases, are called **metallic elements;** those, like phosphorus, whose oxides give acids, are called **non-metallic elements.** The distinguishing words are selected because the division corresponds, in a general way at least, with the separation into two sets to which merely physical examination of the elementary substances would lead.

Hydrates. — Many substances unite with water to give compounds called **hydrates.** Thus if we take zinc sulphate (p. 132) and dissolve it in water and allow the excess of the latter to evaporate,

the solid appears in long transparent crystals. When these are dried with blotting paper and heated in a test-tube, they give off a large amount of steam, the hydrate of zinc sulphate decomposing and leaving *anhydrous* zinc sulphate. The latter, when once more moistened, changes back into the hydrate:

$$ZnSO_4 + 7H_2O \rightleftarrows ZnSO_4,7H_2O.*$$

Many common chemicals are in fact such hydrates. Thus common **blue-stone,** used in gravity batteries, is a hydrate of cupric sulphate, with the formula $CuSO_4,5H_2O$. When heated, it loses water and leaves the colorless, anhydrous cupric sulphate. These are cases of simple combination and decomposition.

That hydrates are regular chemical compounds (although of a more complex nature than any we have discussed in earlier chapters, being formed by the combination of *compound substances,* not of *elements*) is shown by the following two facts: (1) They contain definite proportions by weight of their constituent compounds. Furthermore, the proportions are always such as to represent simple molecular ratios of these compounds. Thus blue-stone, when heated to give anhydrous cupric sulphate, always loses 36.1 per cent by weight of water, no more and no less. This corresponds *exactly,* on examination, to the formula $CuSO_4,5H_2O$. The proportions in solutions, and other physical aggregates, except by chance, cannot be expressed by means of formulæ. (2) A hydrate has physical properties entirely different from those of the water (or ice) and of the other substance used in preparing it. It is a typical compound, formed by the first variety of chemical change (p. 15). Thus, cupric sulphate, often called anhydrous cupric sulphate to distinguish it from the compound with water, is a white substance crystallizing in shining, colorless, needle-like prisms. The pentahydrate (blue-stone or blue vitriol) is blue in color, and forms larger but much less symmetrical (asymmetric or triclinic) crystals (Fig. 27, p. 61): $CuSO_4 + 5H_2O \rightleftarrows CuSO_4,5H_2O$.

Efflorescence. — Some hydrates are so unstable that the water passes off, even at room temperature, when the hydrate is left in

* In the formula for the hydrate of zinc sulphate, it will be seen that we do *not* add together all the atoms of oxygen, and write $ZnH_{14}SO_{11}$. The latter would show the composition of the substance correctly, but it would show *nothing more.* Now chemists find it convenient, frequently, to adapt the formula so that it shall indicate also *some important* chemical property or *reaction* of the substance. Hence the formula $ZnSO_4,7H_2O$, which indicates at a glance the relationship of the substance to zinc sulphate ($ZnSO_4$). The hydrate is *made from* zinc sulphate by adding water, and is easily *decomposed into* these two substances again. The reaction formula hints at this familiar *reaction.* Note, however, that the comma (,) does *not* indicate a *mixture* of the materials, such as $ZnSO_4$ and H_2O, but a single substance composed of both. The plus (+) sign is used between the formulæ of different, uncombined substances in a mixture.

an open vessel. Thus crystals of washing soda $Na_2CO_3,10H_2O$ crumble to powder (**effloresce**) *when not kept in a closed bottle:*

$$Na_2CO_3,10H_2O \rightleftarrows Na_2CO_3 + 10H_2O.$$

If a crystal of a hydrate like this is placed in the barometric vacuum (Fig. 80, p. 166) a considerable vapor pressure of water is indicated, so that the tendency of the hydrate to decompose, when this vapor is allowed to escape, is easily understood. The pressure of water vapor in equilibrium with such hydrates, when partially dehydrated at ordinary temperatures, is found to be *greater* than the average pressure of water vapor in the atmosphere.

On the other hand, when anhydrous cupric sulphate and zinc sulphate, obtainable from the hydrates by heating only, are spread out in the air, they return slowly to the hydrated condition. They combine with the moisture in the air. The pressure of water vapor in the air is greater than the pressure of water vapor in equilibrium with these hydrates and their anhydrous products at ordinary temperatures. Calcium chloride absorbs water vapor practically quantitatively (p. 138), because of its phenomenal tendency to form a hydrate.

Equilibria between Solid and Vapor. — The detailed discussion of the equilibrium conditions between the solid and vapor states, for the particular case of salt hydrates, will be postponed until a later chapter (p. 689), in view of the complexities introduced into the situation through the simultaneous chemical reaction involved. We shall, however, for the sake of completeness, supplement the description of liquid-vapor equilibria at this point by a brief consideration of the equilibrium between solid and vapor in the case where merely a change of state occurs.

The packing of the atoms, or groups of atoms, in a crystal lattice is, generally, even closer than in the case of liquids, and cohesive forces between adjacent particles are much more pronounced. The resistance offered by the atoms in a crystal to forcible changes of position is shown by the very low *compressibility* of matter in the crystalline state. Nevertheless, some degree of *motion* of the particles must still persist, since many crystalline substances show a measurable vapor pressure. Some vapors, indeed (*e.g.*, phosphorus, iodine), can be condensed directly to crystals without passing through the intermediate liquid state.

The results of X-ray work indicate that this motion of the atoms of a crystal consists of *rapid vibrations* about a mean position, the average velocity of the atoms being greater the higher the temperature. Atoms vibrating violently at the surface are evidently exposed to the risk of breaking away altogether, after which they combine to form molecules of liquid or of vapor. Similarly, molecules of liquid or of vapor striking the crystal surface may stick thereto, their constituent atoms arranging themselves in a continuation of the crystal pattern. Equilibrium relations between crystals and vapor

(and also between crystals and liquid) resemble closely, therefore, those between liquid and vapor discussed earlier in the chapter (pp. 169–70), to which reference should here be made.

Reversible Chemical Actions. — The contrary effect upon an unstable hydrate of leaving the bottle in which it is contained open or closed, referred to above (p. 176), deserves a moment's notice. When understood, it explains many things in chemistry. The hydration and dehydration are opposite directions of the same chemical change, and the condensed statements of the actions were written with the **double arrow** to indicate this (p. 173). When the bottle is closed, the water vapor is unable to escape and recombines with any anhydrous particles as fast as other particles of the hydrate decompose. **A reversible action** therefore **cannot complete itself, if the products of the action are kept together and not allowed to separate.** On the other hand, **a reversible action will go to completion if one of the products escapes,** as the water vapor does when the bottle is left open. This idea enables us to answer several interesting questions.

For example, why does steam decompose to the extent of 2 per cent at 2000°, but not any further? All its parts are alike and are therefore equally *capable* of decomposing. The answer is, because neither the oxygen nor the hydrogen is removed, or can easily be removed, from the steam, and so the completion of the decomposition is prevented by continual *recombination of these gases.*

When a reversible action has come to a standstill, we say that **equilibrium** has been reached. This means that two opposing tendencies are neutralizing each other's effects.

When will reversible actions go to completion? The products must be of such a nature that they *separate easily*. In practice this happens when *one is a gas or vapor,* like the water vapor coming from a hydrate, while the other is not. The *settling of one product as a precipitate,* while the other stays in solution, is, as we shall see (pp. 225, 282), another common way in which the separation occurs.

When iron and water are heated in a *closed* vessel, the hydrogen and magnetic oxide of iron which are produced (p. 131) react with each other to give back water and iron:

$$3Fe + 4H_2O \rightleftarrows 4H_2 + Fe_3O_4.$$

In a closed vessel we could never use this method for preparing any quantity of hydrogen. To prepare hydrogen by this action we must leave the tube open, and employ a large excess of steam *to sweep the hydrogen out.* This separates it effectually from the oxide of iron, and prevents the reversal of the action. Devices depending on mechanical principles like this are continually used in chemistry for securing easy methods of preparing substances.

Hydrogen Peroxide. — The chemical behavior of the other compound of hydrogen and oxygen, hydrogen peroxide (see p. 366), is difficult to comprehend until further experience has been gained. Then, too, its formula H_2O_2 cannot be justified until the means of determining molecular weights in solution have been discussed. In view of these facts, it will be taken up later.

Exercises. — 1. Name some other transitions from one physical state to another which are familiar.

2. What evidence is there in the common behavior of ether and chloroform to show that these liquids have high vapor tensions?

3. How many grams of water could be heated from 0° to 100° by the heat required to melt 1 kilogram of ice at 0°?

4. What do you infer from the fact that alum and washing soda lose their so-called "water of crystallization" when left in open vessels, while gypsum does not (p. 176)?

5. Which facts show most conclusively that hydrates are true chemical compounds?

6. In what ways does a hydrate differ from, (*a*) a solution, (*b*) a hydroxide?

7. Should you expect to find any difference, in respect to chemical activity, between the three forms of water (ice, water, and steam)? If so, arrange them in the order of probable increasing activity (compare p. 142). Have we had any experimental confirmation, or the reverse, of this conclusion?

8. Glauber's salt is a hydrate of sodium sulphate Na_2SO_4. If 6 g. of Glauber's salt, when heated, lose 3.36 g. of water, what is the formula of the hydrate?

9. If 50 c.c. of hydrogen and 37 c.c. of oxygen are exploded in a closed tube, which gas remains and what volume of it is left?

10. How many calories of heat would be required to change 5 grams of ice at 0° into steam at 100°?

11. The percentage composition of water by weight is: hydrogen 11.19, oxygen 88.81. The density of oxygen referred to hydrogen as unity is 15.88 (p. 117). Calculate from these data the proportions by volume in which hydrogen and oxygen combine to form water.

12. Given the densities of hydrogen and of oxygen at 0° and 760 mm. (p. 93), calculate the density of steam at 100° and 760 mm.

An accurate experimental determination leads to the value 0.6056 g. per liter. Does this agree with your calculated value? If not, how do you account for the discrepancy?

13. A kilogram of water at 100° and 760 mm. occupies 1043.2 c.c. Using the experimental value for the density of steam given in Exercise 12, calculate how many c.c. of steam would be obtained from 1 c.c. of boiling water (p. 165).

14. What volume of ice at 0° would be obtained by condensing and freezing 1 liter of steam at 100° and 760 mm.?

15. The specific heat of hydrogen at 100° and 760 mm. is 3.40; of steam 0.46. Which requires more heat to raise it from 100° to 101°, a liter of hydrogen or a liter of steam? What are the exact values in each case?

16. Explain how water, even in cold weather, gradually dries up. Why is the evaporation so much more rapid in warm weather? Why does a strong wind hasten the evaporation?

17. Why does a glass full of cold water, when brought into a warm room, sometimes become coated with a film of water on the outside?

18. Explain why we are able to prepare oxygen by heating mercuric oxide (p. 23), in spite of the fact that the action is reversible (p. 88).

READING REFERENCE

Water and its Components. Journal of Chemical Education, 5, 1163, 1928.

CHAPTER XI

MOLECULAR WEIGHTS AND THEIR APPLICATIONS

As we have seen (p. 160), when the *volumes* occupied by substances in the gaseous condition, rather than the weights, are taken as the basis of measurement, the combining proportions are *simple* and are expressible by *small whole numbers* (Gay-Lussac's law). This shows that there must be some relationship, *connected with chemical combination,* between the amounts of *different* substances contained as gases in equal volumes. It suggests that we might do well to take such amounts (weights of equal volumes) as the standard or unit quantities for chemical purposes. Now this is precisely what the chemist has found it in practice most convenient to do, and the present chapter deals with the units of material based upon comparing equal volumes.

Illustrations of Gay-Lussac's Law. — Let us first familiarize ourselves with the volume-measuring point of view in chemical actions. The following are a few observed facts, beginning with the union of hydrogen and oxygen already discussed (p. 160):

(1) Hydrogen (2 vols.) + Oxygen (1 vol.) → Steam (2 vols.).
(2) Hydrogen (1 vol.) + Chlorine (1 vol.) → Hydrogen chloride (2 vols.).
(3) Chlorine monoxide (2 vols.) → Chlorine (2 vols.) + Oxygen (1 vol.).
(4) Mercuric oxide (not volatile) → Mercury (2 vols.) + Oxygen (1 vol.).
(5) Phosphorus (1 vol.) + Oxygen (5 vols.) → Phosphorus pentoxide (1 vol.).
(6) Zinc (at 1000°, 2 vols.) + Sulphur (at 1000°, 1 vol.) → Zinc sulphide (not volatile).

It will be noted that in some cases, like (2), there is no change in the total volume. In others there is a shrinkage, as in (1) and (5). In still others, like (3), where chlorine monoxide decomposes, there is an increase in volume. In (5), in order that all the materials may be gaseous, the whole experiment must be done at a very high temperature (and at some suitable pressure). In (4) the mercuric oxide itself does not become gaseous, but decomposes, so that its own relative volume cannot be given. In (6) the zinc and sulphur can be combined as vapors at 1000°. The product (zinc sulphide)

will not remain gaseous at any temperature at which its volume could be measured, however, and so its volume is not recorded.

It must be kept constantly in mind that the law *applies to volumes in the state of gas or vapor only.* There is no rule about the proportions by volume required for the chemical combination of liquids and solids.

Avogadro's Hypothesis. — We have found (p. 119) that the physical behavior of matter, and particularly of gases, may be explained by the conception that matter is composed of molecules. Now Gay-Lussac's law is a chemical, and not merely a physical fact, yet the molecular hypothesis can explain it also.

Since matter is composed of molecules, a chemical action between two kinds of matter must consist really in an interaction of the molecules of each kind. Molecules of the two kinds must meet and they may then either *combine* to form a compound molecule, or they may *exchange* material in some fashion. Since equal volumes are often the exact quantities required for the action, it appears most likely that **in equal volumes of different gases** (at the same temperature and pressure) **the number of molecules present are equal.** This addition to the molecular hypothesis was first suggested by an Italian physicist, Avogadro (1811). When two gases interact in equal volumes (like hydrogen and chlorine), one molecule of each is all that is required for a small sample of the change in question. Since two volumes of hydrogen are required to unite with one volume of oxygen, clearly the interaction involves two molecules of hydrogen for every one of oxygen. Since two volumes of steam are produced, evidently the two molecules of hydrogen and one of oxygen yield two molecules of water.

This hypothesis of Avogadro helps us to a clearer notion of how these chemical changes take place. The idea that all gases contain equal numbers of molecules in equal volumes also explains why *all* gases behave alike when subjected to equal changes either in pressure or in temperature (Boyle's and Charles' laws, p. 115). No facts which conflict with this hypothesis are known, and all the known facts confirm it. Hence Avogadro's hypothesis, although its recognition by chemists was long delayed, has constituted, since its re-presentation in 1858 by Cannizzaro, one of the most important foundations of chemical theory.

Meaning of Avogadro's Hypothesis. — First, we must understand clearly what is implied in the statement that: In equal volumes of all gases, at the same temperature and pressure, there are equal numbers of molecules. It means that, for instance, at 100°

and 760 mm., in specimens of all gases, the average spacing of the molecules is identical. This condition is independent of the nature of the gas — for example, whether it is a simple or a compound substance, like oxygen and carbon dioxide, respectively, or a mixture, like air. It means that when, at some fixed temperature, we fill the same vessel with a number of different gases or gaseous mixtures succesively, the number of molecules that it will hold at a pressure, say, of one atmosphere will always be the same. If we take care to keep temperature and pressure the same, the equality in the number of molecules that will enter the jar will take care of itself automatically. In what follows, to avoid continual repetition, standard conditions (0° and 760 mm.) are assumed unless other conditions are specifically mentioned.

This statement would be *strictly* true only in the case of gases, if such existed, which behaved in ideal accord with the laws of Boyle and Charles. Since, however, in all gases, with the exception of hydrogen, a certain tendency to cohesion between molecules is distinctly noticeable and its amount varies from gas to gas, the density with which the molecules are packed is not *precisely* the same in any two of them (p. 123). Hence, Avogadro's law is not perfectly realized in any known gases. In the case of hydrogen, for example, a very slight divergence from the behavior of an ideal gas exists, and in the case of chlorine it amounts to about 1½ per cent, and is quite conspicuous. This slight irregularity in the packing of the molecules, however, does not interfere with the practical application of this law in chemistry.

The Standard or Unit Volume. — The volumes in the foregoing paragraphs are simply relative, and the statements are true of gaseous volumes of any actual dimensions (large or small), provided only they bear the proper *relationship,* such as 2 : 1, 1 : 1, or 1 : 5, in each case. An actual value has been chosen, however, for the volume which is the standard or unit in chemistry. This is the volume occupied by 32 grams of oxygen, which is **22.4 liters** at 0° and 760 mm. This volume is equal to that of a cube about 11 inches in height (Fig. 83). At other temperatures and pressures this volume, in order to contain the same amount of material, alters its value, in accordance with the laws of Boyle and Charles (p. 115). The reason for selecting this par-

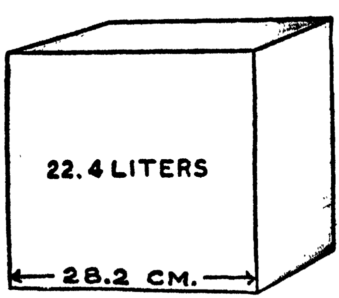


FIG. 83. The Gram-Molecular Volume at 0° and 760 mm.

ticular volume will be readily seen, so soon as we shall have presented and discussed in detail the actual weights of various materials which fill it.

Consequences of Avogadro's Hypothesis: Molecular Weights. — Equal volumes of the *same* gas (at the same temperature and pressure) have equal weights. But equal volumes of *different* gases have different weights. The differences are often very great. Thus, volume for volume, oxygen is sixteen times as heavy as hydrogen, and mercury vapor one hundred times as heavy. Now, if equal volumes of different gases contain equal numbers of molecules, these differences must be due to the differing weights of the several kinds of molecules. Thus, measuring the weights of equal volumes of different gases will give us the relative weights of their molecules. For example, since 22.4 liters of oxygen weigh 32 g., while the same volume of hydrogen weighs 2.016 g. and of water vapor 18.016 g., and these are the weights of equal numbers of molecules, the individual molecules must differ in weight in the ratio 32 : 2.016 : 18.016. These are the relative weights of the three kinds of molecules. In chemistry the weights in grams of 22.4 liters (at 0° and 760 mm.) of various gases are called the **molecular weights** of those gases. The unit volume, 22.4 liters, is called the **gram-molecular volume** (G.M.V.).

The number of molecules actually contained in the G.M.V. has been determined by several independent methods, the agreement of the results obtained furnishing very strong support for the validity of the molecular hypothesis. The value at present accepted as most accurate is that of Millikan, 6.06×10^{23} (see footnote on p. 64). It is of importance that the student should obtain some idea of the significance of this stupendous number, which he has already encountered once before (p. 73), in order to appreciate more clearly the detailed discussion of the properties of gases in an earlier chapter (pp. 119–25). Imagine a G.M.V. of a gas at 0° and 760 mm. to be divided equally among the inhabitants of the United States (say 130,000,000). Each person would receive about one-fifth of a cubic millimeter as his share. Imagine, further, that the market price of a million molecules of this gas was one cent. Few of the recipients would think it worth while to cash in their microscopic sample; those doing so, however, would benefit to the extent of about 50 million dollars!

A common question is: Do not molecules of different substances differ in size, and will not the numbers required to fill the G.M.V. therefore be different? The answer is that the molecules are all so small compared with the spaces between them (at 760 mm.) that the distances from surface to surface are practically the same as from center to center. A G.M.V. of oxygen, when liquefied, gives less than 32 c.c. of liquid oxygen, or less than 1/700 of the volume as gas. It is only when gases are so severely compressed that the

nearness of the molecules to one another approaches that found in the liquid condition that the effects of the bulk of the molecules become conspicuous, and a difference in the behavior of different gases is noticeable. But in the work discussed in this chapter, pressures over one atmosphere are intentionally avoided.

The student is specifically warned against the very common error of assuming that the size of the hydrogen molecule, for example, is much less than that of the oxygen molecule, *because* its mass is much smaller. There is *no general connection* between the weight and the size of molecules. Whatever the weight, the actual size is insignificant, under standard conditions, compared with the free space.

Measurement of Molecular Weight. — The molecular weight of any gas is *measured* by weighing any convenient volume and calculating by proportion the weight of 22.4 liters. If the gas or vapor was not measured at 0° and 760 mm., the measured volume must be reduced by rule to standard conditions before the weight of 22.4 liters is calculated.

For example, 190 c.c. of a gas at 0° and 760 mm. weigh 1.23 g. If x be the weight of 22.4 liters (= 22,400 c.c.),

$$190 : 1.23 :: 22{,}400 : x \ (= 145 \text{ g.}).$$

Again, 210 c.c. of a vapor at 100° and 743 mm. weigh 1.12 g. This volume at 0° and 760 mm. would become:

$$210 \times \frac{273}{373} \times \frac{743}{760} = 150.3 \text{ c.c.}$$

and

$$150.3 : 1.12 :: 22{,}400 : x \ (= 167 \text{ g.}).$$

The various scales on which the densities of gases (see p. 117) are most frequently calculated are illustrated in the table, page 185.

The values for water (b.-p. 100°), mercury (b.-p. 357°), and mercuric chloride (b.-p. 307°) are measured at high temperatures and reduced by rule (p. 115) to 0° and 760 mm. Although these three substances do not actually exist in the state of vapor at 0° and 760 mm., the results so obtained are just as significant as those for less easily condensible gases. The molecular weight of any substance which can be vaporized *under any conditions,* indeed, can be determined by this method (see p. 118).

All the figures in the first two columns, as they stand, are purely physical in derivation. The values in the third column, however, are of greater significance, in view of the fact that they are based upon a definite chemical unit — the volume occupied by 32 grams

	Weight of One Liter, 0° and 760 mm.*	Density, Air = 1	Molecular Weight, Oxygen = 32
Hydrogen	0.0899	0.0696	2.016
Oxygen	1.429	1.105	32.00
Chlorine	3.166	2.449	70.92
Hydrogen chloride	1.628	1.259	36.468
Carbon dioxide	1.965	1.520	44.00
Water	0.8045	0.622	18.016
Mercury	8.957	6.908	200.6
Mercuric chloride	12.121	9.354	271.52
Air	1.293	1.00	28.955

of oxygen at 0° and 760 mm., or the gram-molecular volume. Our *chemical* scale of densities is therefore calculated to the scale **density of oxygen** = 32. The final column of the table shows the results of recalculating the densities to this chemical scale.

We multiply the weight of a liter of any given gas by 22.4 to get the **gram-molecular weight** of the substance. The term gram-molecular weight being somewhat ponderous, we often abbreviate it to **molar weight,** and still further to **mole.** Thus, a mole of chlorine is 70.92 g. of the element, and a mole of hydrogen chloride is 36.468 g. of the compound.

Final Justification of Atomic Weights.—If the paragraphs dealing with combining proportions are now reread (pp. 45-51), it will be found that the foundations for a system of atomic weights were there worked out, but that no basis for *definitely fixing* the individual values was discovered. Later on, it was shown that a definite choice between the different values suggested by combining proportions for the atomic weight of any given element could be made by means of the law of Dulong and Petit (p. 57), and also that information regarding the actual weight of the individual atoms could be obtained by analyzing crystal lattice structures (p. 73). The theoretical vindication of Dulong and Petit's law and the study of crystal lattices represent, however, comparatively recent advances in chemistry, and it remains therefore for us to

* In practice, owing to the fact that Boyle's and Charles' laws do not describe the behavior of any known gas *exactly* (they apply only to a "perfect" gas), certain additional, small corrections have to be applied when very precise values are required. It may be noted that, in order to make the fundamental significance of the numerical data presented in the preceding pages immediately intelligible to the beginner, all of the gases so far considered have been *assumed* to be "perfect." The actual experimental values differ only very slightly from those given.

demonstrate here how final atomic weight values have been derived independently by a most valuable and longer-accepted method, based upon the determination of molecular weights.

To establish atomic weights by this method, the plan of procedure is perfectly simple. We imagine ourselves filling the cube (Fig. 83) with one gaseous compound after another, and in each case determining by analysis the weight of each constituent element present in a cube-full of the substance. Two experimental operations are necessary with each substance:

First we **determine the density,** and this gives us the gram-molecular weight, *i.e.*, the amount filling the cube. This shows the relative weight of a molecule of the substance, as compared with that of one molecule of oxygen.

Second we **determine the percentage composition of the substance,** and use our result to apportion the total gram-molecular weight of the substance among its constituent elements. This, in turn, shows the weight of the quantity of each element present in each molecule, relative to the weight of a molecule of oxygen.

For example, the cube holds 36.468 g. of hydrogen chloride, and this amount, when decomposed, yields 1.008 g. of hydrogen and 35.46 g. of chlorine.

Finally, to determine the atomic weight for a given element, we repeat the two foregoing operations with as many different compounds of the element as possible, and then we examine the various quantities of the element found in the G.M.V. of the various compounds. From inspection of these quantities we quickly select the value of which all are multiples, by unity or some integral number. This value is the one accepted as the atomic weight, since it represents the weight of one atom of the element, compared with the weight of a molecule of oxygen, and molecules containing more than this proportion contain two, three, or more atoms of the element.

Some Illustrations. — For example, if we are seeking the atomic weight of chlorine, we set down the result for hydrogen chloride just given. Then we take another compound of chlorine, say phosphorus oxychloride (a liquid). We determine the weight of a measured volume of its vapor, at a properly chosen temperature and pressure, and the result gives us, by calculation, the molecular weight, viz., 153.41. That is, 153.41 g. of the substance would fill the cube, if it could be kept as vapor at 0° and 760 mm. And this amount of the substance is found by analysis to contain 31.03 g. of the element phosphorus, 16 g. of the element oxygen, and

106.38 g. of the element chlorine. We then continue the processes described, using all the conveniently volatile compounds of chlorine. When we have studied as many compounds as possible in this way, we find that there are different quantities of chlorine in our list, *but they are all integral multiples of* 35.46 *g.* In phosphorus oxychloride, for example, the quantity was 106.38, or 3 × 35.46. Hence

Substance	Molar Weight	Weights of Constituents in Molar Weight						
		Hydrogen	Chlorine	Oxygen	Phosphorus	Carbon	Mercury	Molecular Formula
Hydrogen chloride	36.468	1.008	35.46	....	......	....	.....	HCl
Chlorine dioxide	67.46	......	35.46	32	......	....	.....	ClO_2
Phosphorus trichloride	137.41	......	106.38	....	31.03	....	.....	PCl_3
Phosphorus oxychloride	153.41	......	106.38	16	31.03	....	.....	$POCl_3$
Phosphorus pentoxide	284.12	......	......	160	124.12	....	.....	P_4O_{10}
Phosphine	34.054	3.024	......	....	31.03	....	.....	PH_3
Water	18.016	2.016	......	16	......	....	.....	H_2O
Methane	16.032	4.032	......	....	......	12.0	.....	CH_4
Acetylene	26.016	2.016	......	....	......	24.0	.....	C_2H_2
Propane	44.064	8.064	......	....	......	36.0	.....	C_3H_8
Formaldehyde	30.016	2.016	......	16	......	12.0	.....	CH_2O
Acetic acid	60.032	4.032	......	32	......	24.0	.....	$C_2H_4O_2$
Mercurous chloride	236.06	......	35.46	....	......	....	200.6	$HgCl$
Mercuric chloride	271.52	......	70.92	....	......	....	200.6	$HgCl_2$

35.46 g. is taken as the unit quantity, the **atomic weight** of the element chlorine.

In the **table** presented immediately above, a few **sample results of the process just outlined** are given. The first column contains the molar weight, *i.e.*, the weight of the substance which occupies the G.M.V. cube. In the other columns are entered the weights of the various elements which together make up the total molar weight.

To contain similar data for all the volatile compounds of every known element, a huge table, of which this might be a small corner, would be required. With such a table at hand, the atomic weight of each element could promptly be picked out. Thus, in the carbon column it would be found that all the weights of carbon were either 12.0 or integral multiples of 12.0, and this is therefore the atomic weight of carbon. Similarly the atomic weight of oxygen is 16, of phosphorus 31.03, of mercury 200.6, and so on.

When the atomic weights have finally been selected, we can go through the table and change all the numbers into multiples of the chosen atomic weights. Thus, for 70.92 we write 2×35.46, and for 106.38 we write 3×35.46, and so forth. The reader should prepare such a modification of the table. With this new form of the table before us, we can, finally, replace the atomic weights by the symbols which stand for them, writing, for 35.46, Cl, for 2×35.46, Cl_2, and so forth. The results of doing this in each line, *i.e.*, for each substance, are collected at the ends of the lines in the last column of the table. The reader should himself repeat the substitutions of the symbols, and so verify the formulæ given. These formulæ, since they are based on the molecular weights, in such a way that when the numerical values are substituted for the symbols the total restores to us the molecular weight, are called **molecular formulæ** (compare p. 79).

Of course, an element *might* be encountered of which no volatile compound containing the smallest possible weight was yet known. If methane and formaldehyde were still undiscovered, and only the other three compounds containing carbon in the above table were available, we should then have to take the greatest common measure of 24.0 and 36.0, namely 12.0, as the logical unit for carbon.

The chemical unit weight or atomic weight of an element may thus be defined as: The **G.C.M.** (greatest common measure) **of the weights of that element found in the molar weights of all its volatile compounds.**

Further Comments on Atomic Weights. — The fact that *all* the numbers in any one column of the table (p. 187) turn out to be even multiples of a single number need not seem mysterious. The molecule of every compound containing chlorine must contain one, two, three, or some other *whole* number of chlorine atoms, for chlorine, like all other elements, does not furnish fractions of atoms in any cases of combination. Now, the weight of chlorine in 6.06×10^{23} atoms, assuming one atom of chlorine to each of the 6.06×10^{23} molecules present in 22.4 liters, must be 35.46 g. Hence, if the weight of chlorine in 22.4 liters of any compound differs from 35.46 g., it can do so only because there are two atoms of chlorine per molecule, giving 2×35.46 g., or three atoms giving 3×35.46 g. of chlorine, and so forth. Thus the quantities of chlorine in the G.M.V. of *all* compounds of chlorine must be multiples of 35.46 by unity or some other integer.

It is hardly necessary to add that the atomic weights, found as described above, are equally serviceable in expressing the compositions of compounds which are *not* volatile. The atoms in non-

volatile compounds are identical in properties with the atoms of the same elements in volatile compounds. If an element gives no volatile compounds, other methods of fixing its atomic weight are available (see pp. 57, 448).

Distinction between Atoms and Molecules. — At this point it is profitable to attempt to remove any confusion which the student may have in his mind with respect to the two conceptions of *atoms* and of *molecules*, as applied to elementary substances such as oxygen. In the kinetic-molecular hypothesis we defined the molecules of a gas as exceedingly small particles, all alike in mass, separated from one another and in rapid motion. In the atomic theory, atoms are defined as the ultimate particles of an element, also all alike in mass, by the coördination of which with the ultimate particles of other elements compounds of definite composition are produced.

That the atom and the molecule are *not identical* in the case of gaseous oxygen will be evident from the fact that, in the development of molecular weights, we employed oxygen = 32 as our standard, while for the atomic weight of oxygen we have arrived at the value 16. In other words, while 22.4 liters of oxygen at 0° and 760 mm. weigh 32 grams, volatile compounds of oxygen (such as phosphorus oxychloride and water) are known, which contain as gases only 16 grams of oxygen in 22.4 liters (reduced to 0° and 760 mm.). Now equal volumes of all gases under the same conditions contain equal numbers of molecules (Avogadro's law). Hence we are forced to the conclusion that the weight of oxygen in a molecule of oxygen must be twice the weight of oxygen in a molecule of vaporized phosphorus oxychloride or water. But the molecules of these compounds must contain at least one atom of oxygen, since atoms are indivisible. Consequently the molecule of oxygen in the gaseous state must contain at least two atoms of oxygen. We have no reason for believing that it contains more than two, since we know of no volatile compounds which contain less than 16 grams of oxygen in their gram-molecular volume. The molecule of oxygen is therefore regarded as **diatomic**, or as consisting of two atoms in intimate conjunction.

The simple fact that hydrogen and oxygen, when mixed, do not combine (p. 139) may assist in reconciling us to the diatomic nature of their molecules. Some part of the mixture has to be heated strongly to start the interaction. Now the molecular formulæ, H_2 and O_2, suggest that each gas is really in combination already (with itself), and they therefore explain to some extent the

indifference of the gases towards one another. If the molecules were free atoms, they could not encounter one another continually as they move about, and yet escape combination as we observe that they do. We may imagine that the primary effect of heating is to decompose some of the molecules, and liberate hydrogen and oxygen in the atomic condition, and that the combination of these atoms starts the explosion of the whole mass.

In the case of hydrogen, the diatomic nature of the molecules has been demonstrated by an entirely different method by Langmuir. It has already been mentioned (p. 138) that a wire raised to a white heat in air by means of an electric current, cannot even be kept at a red heat by the same current in hydrogen. To raise the wire to a white heat in hydrogen, a much heavier current must be applied. In air, heat from the hot wire is used up solely in accelerating the motion of the molecules of the gas. Langmuir has shown, however, that in hydrogen, additional heat is consumed in causing decomposition of many of the diatomic molecules into single atoms:

$$H_2 \rightleftarrows 2H.$$

He has measured the percentage of molecules dissociated (at 760 mm.), and found that it varies from 0.33 per cent at 2000° to 13 per cent at 3000° and 34 per cent at 3500°. When the temperature falls, the atoms re-combine to diatomic molecules.

When we come to compounds, of course, the distinction between atoms and molecules is much more evident.

The molecule is here necessarily a complex unit, built up by the association of the atoms of the constituent elements into definite groups. Each group contains a fixed *integral* number of the atoms of each element, and the *proportions* in which these integers stand in any given compound may be calculated from the composition of the compound by weight (p. 78). To find the actual molecular unit (*i.e.*, the *absolute* number of atoms of each element contained in the molecule) a molecular weight determination is necessary, as will be illustrated below.

Significance and Use of Molecular Formulae. — In an earlier chapter (p. 77) we have already made particular note of the fact that the formula must represent the weight of the chemical unit quantity of the substance, as well as its composition. We now see that the total weight, for which the symbols in a formula stand, must be equal to the weight of the substance occupying the gram-molecular volume. In other words, the *formula-weight* must represent one cube-full (Fig. 83, p. 182) of the substance.

If the molecular formulæ deduced for the compounds in the table on p. 187 be now examined, however, it will be observed that several of these are not in their simplest terms. Thus, the formula

of acetylene is C_2H_2. The formula CH would represent the composition of the substance equally well, for 12.0 : 1.008 is the same as 24.0 : 2.016. But the formula CH gives a total of only 13.008, while C_2H_2 shows the total weight of the molecule to be 26.016 and is in accordance therefore with *the weight of the G.M.V.*, as well as with the composition of the substance. Similarly the molecular formula of acetic acid is $C_2H_4O_2$, and not the simpler, identical proportion CH_2O. The latter is the molecular formula of a totally different substance, formaldehyde, now much used as a disinfectant. The vapor of this substance has only half the density of acetic acid vapor, and this fact, recorded in the formula, helps to remind us that the substances are different. Still another substance of the same composition is grape sugar (glucose), $C_6H_{12}O_6$.

Molecular formulæ like C_2H_2 and $C_2H_4O_2$ are easily interpreted in terms of the atomic hypothesis. C represents one atom of carbon and H one atom of hydrogen. But there is no reason why a molecule of acetylene should not contain two atoms of each kind. Similarly, the molecule of formaldehyde contains four atoms (CH_2O), and one of acetic acid eight atoms ($C_2H_4O_2$), and one of glucose twenty-four atoms ($C_6H_{12}O_6$), although the relative numbers of each kind are the same. Indeed this hypothesis helps to clear the matter up, for chemists go so far as to account for the chemical behavior of the substances by an imagined geometrical arrangement of the atoms in their molecules, and these three kinds of molecules behave as if they differed in structure as well as in the number of atoms they contain.

In the cases of tin oxide (SnO_2) and ferric oxide (Fe_2O_3), we have substances which cannot be converted into vapor or dissolved (see p. 215), so that their molecular weights are unknown (for non-polar involatile substances, however, see p. 71). *In such cases, we use for convenience the simplest formula* that will show the correct proportions.

Applications: Interactions between Gases. — According to Avogadro's law, if we filled a succession of vessels of equal dimensions with different gases, and could arrest the motion of the particles and observe their disposition, we should find that the average distance between particle centers would be essentially the same in all cases. This would be true whether our vessels were filled with single gases, with homogeneous mixtures, or with gases in layers. Such being the case, if any chemical change is brought about in the mass which results in a multiplication of the molecules, it is evident that the volume will have to increase in order that the spacing may remain the same as before. If any chemical action results in a diminution of the number of molecules, then a shrinkage must take place in order that the spacing may be preserved as before. Thus, in a mixture of hydrogen and oxygen, according to our

hypothesis, when interaction occurs, the following change takes place between neighboring molecules:

$$HH + OO + HH \text{ becomes } HOH + HOH.$$

Since the oxygen molecules, which form a third of the whole, "disappear" within the molecules of hydrogen, the tendency to preserve spacing results in a diminution of the volume by one-third (p. 160). Thus Gay-Lussac's law would have followed as a natural inference from Avogadro's law, if the former, being more obvious, had not been discovered first.

If each of the following squares represents a small volume containing 1000 molecules of gas, then 2000 molecules of hydrogen and 1000 molecules of oxygen give 2000 molecules of water vapor. We may note again, in passing, that, since each molecule of water must contain at least one atom of oxygen, at least 2000 atoms of oxygen were required, and must have been furnished by the 1000 molecules of oxygen. Each of these molecules must therefore have split into two atoms.

Hydrogen 1000 mols.	+	Hydrogen 1000 mols.	+	Oxygen 1000 mols.	→	Water vapor 1000 mols.	+	Water vapor 1000 mols.

This method of looking upon chemical interactions between gases gives us the nearest sight which we can have of the behavior of the molecules themselves. We cannot perceive the individual molecules, but, in consequence of the spatial arrangement which they observe, the change of the whole volume of a large aggregate of molecules enables us to draw conclusions at once in regard to the behavior of the single molecules in detail.

Applications: Molecular Equations. — To utilize the foregoing considerations, chemists **always employ in their equations the molecular formulæ** for the gases and the easily vaporized substances concerned. Thus, if we used the equation:

	$2H$	+	O	→	H_2O
WEIGHTS:	2×1.008		16		18.016

the information it contained would be exhausted when we had placed below the symbols the weights for which they stood. But the molecular equation is much more instructive. The following

shows **the interpretations to which the molecular equation is subject:**

	$2H_2$	$+$ O_2	$\rightarrow$ $2H_2O$
WEIGHTS:	2×2.016 g.	32 g.	2×18.016 ($=36.032$) g.
VOLUMES:	2×22.4 liters	22.4 liters	2×22.4 liters
MOLECULES:	2	1	2

The weights, although doubled, show the same proportions, so that questions of weight are answered as easily as before. These weights, however, being molecular weights, or multiples thereof, can be translated at once into *volumes,* and **questions about volumes can also be answered.** Finally, **the relative numbers of each kind of molecule can be read from this equation,** for the coefficients in front of the formulæ represent these numbers. Where no coefficient is written, 1 is to be understood.*

Applications: To Cases of Dissociation. — Certain gases or vapors yield abnormally small values for their densities, and therefore for their molecular weights derived by reducing these density values to standard conditions (22.4 l. at 0° and 760 mm.), when examined at higher temperatures. This indicates that the molecules have become lighter, and can only mean that decomposition has taken place in consequence of the heating. Behavior of this kind is shown both by compounds and by simple substances.

For example, phosphorus pentachloride PCl_5, although a solid, can be converted into vapor without much difficulty. Its molecular weight, if it underwent no chemical change during the volatilization, would be $31 + 177.3 = 208.3$. The density actually observed at 300° and 760 mm. pressure gives by calculation a molecular weight not much more than half this value. The direct inference from this is that the molecules have not much more than half the weight that we expected; or, in other words, are almost twice as numerous as we expected. The explanation is found when we examine the nature of the vapor more closely. We find that it actually contains very little phosphorus pentachloride, but is almost entirely a mixture of phosphorus trichloride and free chlorine, resulting from a chemical change according to the equation: $PCl_5 \rightleftarrows PCl_3 + Cl_2$. The low value of the density thus tells us

* The application of these properties of molecular equations is illustrated in Chap. XIV (pp. 249–51). If desired, these applications may be taken up after the next section.

that dissociation has taken place. From the value of the density at various temperatures and pressures, we may even calculate the proportion of the whole material which is dissociated under any given conditions. At 300° it is 97 per cent; at 250°, 80 per cent; and at 200°, 48.5 per cent (under a pressure of 760 mm.). Thus, when the temperature is lowered, progressive recombination takes place and the proportion dissociated becomes less. Finally the vapor condenses and yields the original solid.

Again, sulphur boils at 445°, but can be vaporized at a temperature as low as 193°, under very low pressure. At this temperature the density of the vapor gives the molecular weight 256 ($=8 \times 32$) and the molecular formula S_8. At 800°, however, the molecular weight indicated by the density is only one-fourth as great, and the molecular formula is accordingly S_2. At 1700° the molecular formula is still S_2, so that this represents the limit of dissociation: $S_8 \rightleftarrows 4S_2$. When the vapor is cooled, the molecular weight derived from density determinations increases once more and at 193° recovers completely the greater value. Similar observations show that phosphorus vapor at 313° is all P_4, but at 1700° and 760 mm. one-half of the molecules are P_2. Iodine vapor, up to 700°, is all I_2. Beyond this temperature the density diminishes abnormally, and when 1700° is reached the vapor is all I. Thus the molecules are diatomic at low temperatures and monatomic at high ones. The densities of oxygen, hydrogen, and chlorine vary quite normally, in accordance with the gas laws, on heating to 1700°, so that their diatomic molecules exist from temperatures far below 0° up to 1700°, and are evidently very stable. For observations on hydrogen above 1700°, however, see p. 190.

Finding the Atomic Weight of a New Element. — By way of reviewing the fundamental principles explained in this and preceding chapters, let us apply them to the imaginary case of a newly discovered metallic element X. The bromide of the element is found to be easy of preparation and to be volatile. Analysis shows that it contains 30 per cent of the element (and therefore 70 per cent of bromine), and its vapor density referred to air is found to be 11.8. The analysis can always be made much more accurately than the measurement of vapor density, so that the former number is more trustworthy than the latter.

To find the **equivalent** of the element, that is, the amount combined with 79.92 parts (the atomic weight) of bromine, we have the proportion $70 : 30 :: 79.92 : x$, from which $x = 34.3$. The atomic weight must be this, or some small multiple of it (see p. 153).

The G.M.V. of air weighs 28.955 g. (p. 185). Hence the same volume of the vapor of this bromide, which is 11.8 times as heavy as air, will weigh 28.955×11.8 or 341.67 g. This is therefore the

approximate molecular weight of the compound, and 30 per cent of this must be apportioned to the new element:

$$341.67 \times 30 \div 100 = 102.5.$$

The approximate atomic weight of the new element is consequently 102.5, or some *sub-multiple* of 102.5. More exactly, as stated above, it is 34.3, or some *multiple* of 34.3. Evidently the only two possible values for the correct atomic weight are 34.3 and $3 \times 34.3 = 102.9$, the difference between the latter figure and 102.5 being due to error in determining the density, or to deviation from the gas laws (footnote, p. 185). The value 34.3, however, would lead to the formula X_3Br_3 for the bromide, and no compounds of this type are known to exist. So long as no other volatile compound conflicts, then, we adopt 102.9 as the atomic weight. The rest of the molecular weight (238.8 parts $= 3 \times 79.92$) is bromine. Thus the formula of the compound is XBr_3, and from this we see that the element is **trivalent.**

In case no volatile compound of the element can be formed, the weight combining with 79.92 parts of bromine is measured as before. Then some of the free simple substance is made, say by electrolysis, and its specific heat is determined. The sp. ht. is about 0.063. Application of Dulong and Petit's law then gives the atomic weight. The product 34.3×0.063 is equal to 2.161. Hence, the equivalent must be multiplied by 3 to give the atomic weight, for this raises the product to 6.48, which is within the limits indicated by Dulong and Petit's law. Thus the value of the atomic weight is 102.9, as before.

Exercises. — 1. State the change which takes place in the total volume of the gases or vapors in each of the six actions mentioned, p. 180.

2. If 1 liter of nitrogen at 0° and 760 mm. weighs 1.251 g., what is the molecular weight?

3. Calculate the molecular weight of a gas, 200 c.c. of which at 0° and 760 mm. weigh 2.1 g.

4. Find the molecular weight of a gas, of which 250 c.c. at 18° and 752 mm. weigh 2.5 g. (p. 184).

5. The weight of 1 c.c. of sulphur dioxide is 0.00286 g. at 0° and 760 mm. What is its molecular weight?

6. The density of a gas, air = 1, is 2.3. What is its molecular weight?

7. What would be the volume of the G.M.V. under the following conditions: (*a*) 100° and 760 mm., (*b*) 0° and 380 mm., (*c*) 68° F. and 770 mm., (*d*) 0° Abs. and 760 mm.?

8. A bulb containing air at 0° is evacuated by means of a series of pumps until the pressure is reduced to one-millionth of a millimeter. How many molecules remain in 1 c.c. of the "vacuum" thus produced?

9. What would be the volume occupied by 1 g. of carbon tetrachloride (mol. wt. 153.84) in the vapor state at 0° and 760 mm.?

10. 287.5 c.c. of benzene vapor, measured at 100° and 752 mm., weighed 0.725 grams. What is the molecular wt. of benzene?

11. 0.454 g. of acetone vapor were found to occupy a volume of 265.4 c.c. at 75° and 640 mm. pressure. What is the molecular wt. of acetone?

12. A test tube containing potassium chlorate weighed 30.364 g. The oxygen driven off on heating displaced 380 c.c. of water. The temperature was 20° and the barometric pressure 750 mm. What should be the weight of the tube after heating? Assuming that decomposition was complete, what weight of potassium chlorate did the tube contain?

13. If the molecular weight of oxygen had been taken as 100, what would be the volume of the G.M.V. at 0° and 760 mm.?

14. If you were to take a liter flask full of water, tag all the water molecules, empty the flask into the ocean, wait until its contents had become thoroughly mixed with all the water in the world, fill the flask again with water, and count the number of tagged molecules present, how many would you find? For the amount of water in the world the approximate value 1.5×10^{24} c.c. may be employed.

15. The chloride of a new element contains 38.11 per cent of chlorine and 61.89 per cent of the element. The vapor density of the compound referred to air is 12.85. What is the atomic weight of the element, so far as investigation of this one substance can give it (p. 194)? What is its valence?

16. The following are the molecular weights of some compounds of sulphur, with the percentage by weight of sulphur in each:

Compound	*Mol. Wt.*	*Percentage Sulphur*
Hydrogen sulphide	34.08	94.06
Sulphur trioxide	80.06	40.04
Sulphur monochloride	135.04	47.48
Carbon disulphide	76.12	84.24
Mustard gas (p. 655)	158.98	20.16

Calculate the atomic weight of sulphur from these data.

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CHAPTER XII

SOLUTION

The property that many substances have of dissolving in others is a most interesting and valuable one. The value lies chiefly in the fact that some substances are easily soluble in a given liquid and others are, practically, not soluble in it at all. These differences in solubility enable us to accomplish, both in the laboratory and in chemical industry, many things otherwise impossible. Thus, we separated sulphur from iron (p. 21), by using carbon disulphide (CS_2) to dissolve the former. In the same way the *refining of silver* (its separation from the lead in which it is contained) is carried out on a large scale in actual practice by the use of *molten zinc* as a solvent.

Solution. — We distinguish carefully between a solution and a mere mixture, also between a solution and a compound.

A mechanical *mixture*, such as that of iron and sulphur, can never be perfect, as will be evident from what has been said in an earlier chapter (p. 69). However finely we may powder up such a mixture, we cannot possibly bring about a sufficiently intimate dispersion of the particles of its components among one another to justify us in believing that the whole mass has become homogeneous in its ultimate structure. In any true *solution*, however, intermingling of the particles of the separate components down to molecular magnitudes has actually been accomplished. In a solution of sugar in water, for example, the dissolved substance is completely and permanently dissipated throughout the liquid. However long the solution is allowed to stand, sugar never settles out. Only by evaporating off all the water can a complete separation be effected.

Practically speaking, there is no limit to the amount of dissipation which may thus be produced. Thus a single small crystal of potassium permanganate, a common disinfectant which gives

a very deep purple solution in water, may be dissolved in a liter or even in a hundred liters of water, and the purple tinge which it imparts to the liquid will still be perfectly perceptible in every portion of the solution. We may note here the distinguishing characteristic of a solution as opposed to a *compound*. Compounds contain definite proportions by weight (p. 42) and simple atomic ratios (p. 55) of their constituent elements. The composition of a *solution*, on the other hand, can within certain limits (see p. 199) be varied continuously.

Sometimes, when we shake up a finely-divided solid with a liquid, the latter becomes dull, or cloudy, or muddy. The solid particles are here simply suspended in the liquid, not dissolved, and will eventually settle out. Sand, shaken with water, settles at once. Flour, mixed with water, settles more slowly. The particles of flour can be readily separated from the water, however, by filtration (p. 21), the flour remaining on the paper while the water runs through. Such mixtures are called **suspensions.**

In exceptional cases, the subdivision of a suspended substance in a liquid, while not approaching molecular magnitudes, is so minute as to make its retention by filter-paper impossible, or even to prohibit it from settling out in any reasonable time. Solutions of soap, starch and gelatine in water are of this nature. Such suspensions are known as **colloidal suspensions.** To the unaided eye they appear to be true solutions. Their main properties, however, are essentially different from those of true solutions, as will be seen later (pp. 641-2).

Milk owes its cloudy, white appearance largely to droplets of oily matter, which reflect much light from their surfaces. They pass easily through filter-paper. But when milk is allowed to stand they slowly rise to the top, being lighter than the water in which they are not dissolved, but suspended. A mixture of two *liquids* of this nature is called an **emulsion.**

The characteristics, therefore, **of a true solution** are **absence of settling or separation, homogeneity, and extremely minute subdivision (down to molecular magnitudes) of the dissolved substance.**

Chemists commonly call the dissolved substance the **solute** and the substance in which it is dissolved the **solvent.** In many cases, however (when we take two liquids such as alcohol and water, for example), the terms solvent and solute are interchangeable. Gases, liquids, and solids may all be solutes, and dissolve in suitable

gaseous, liquid or solid solvents. In the present chapter only liquid solvents will be considered, and most attention will be paid to water.

Solvents. — Water is by far the commonest and most useful solvent. Very many inorganic substances dissolve in it easily. The fact that many (like sulphur and sand) do not, enables us to separate the components of a mixture containing a soluble and an insoluble substance.

Many organic substances, such as fats, paraffin, petroleum, tar, rubber, cotton, paper, shellac, and so forth do not dissolve to any measurable extent in water. But fats dissolve readily in ether ($C_4H_{10}O$), in carbon disulphide (CS_2), in carbon tetrachloride (CCl_4), and in chloroform ($CHCl_3$). For this reason these substances remove grease which has accidentally got into cloth. Paraffin, petroleum, and tar dissolve in gasoline (petrol), and in benzene (C_6H_6). Cotton and pure paper (like filter paper) will dissolve in concentrated zinc chloride solution (p. 600). Alcohol (C_2H_6O) dissolves shellac (to make varnish).

Again, water dissolves little carbon disulphide, chloroform, carbon tetrachloride, gasoline or benzene. But it dissolves alcohol in any amount, and ether in limited quantity. Some organic substances, like sugar, dissolve easily in water, but hardly at all in other common solvents. Hence candy or molasses can be taken out of cloth by water, but not by solvents for fats.

Saturation. — As a rule, not more than a certain amount of a large bulk of solute is dissolved by a given limited quantity of the solvent. By shaking excess of the solute in a finely divided state with the solvent for a sufficient length of time, this maximum amount will finally be dissolved. The solvent is then said to be **saturated** by the solute in question. Thus, 100 c.c. of water at 18° will dissolve as much as 6.6 g. of potassium chlorate, but not more. The same amount of water will dissolve 213.4 g. of silver nitrate, however, before the solvent becomes saturated. On the other hand, a saturated solution of chalk or marble (calcium carbonate) in water will contain only 0.0013 g. in 100 c.c.

To describe these cases we should say that potassium chlorate is only moderately soluble in water, silver nitrate very soluble, and marble **insoluble.** No substance is *absolutely* insoluble, but for the sake of brevity we call substances like chalk "insoluble" because in most connections they may be so considered.

The number of grams of the solute required to saturate a fixed *volume* or a fixed *weight*, say 100 c.c. or 100 g., of the solvent we call the **solubility** of the substance (at the existing temperature). **The solubilities** at 18° of **one hundred and forty-two substances in**

100 c.c. of water are given in a **table** printed **inside the cover, at the front of this book.** A few additional examples are given below (p. 205).

In some cases there is no limit to the solubility, and therefore no possibility of the solution reaching saturation. Thus alcohol or glycerine and water will dissolve in one another in any proportion. Such pairs of substances are said to be **miscible in all proportions.**

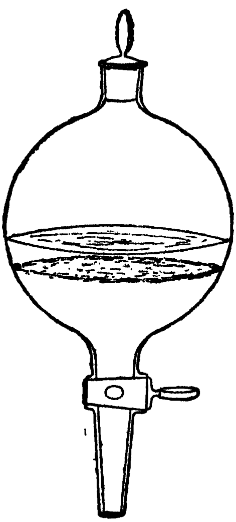


FIG. 84. Partial Miscibility of Ether and Water.

Dilute and Concentrated Solutions. — A **dilute** solution is one containing little dissolved matter, whether the matter is naturally very soluble or not. A **concentrated** solution is one containing much of the dissolved substance, and such a solution can be made with very soluble solutes only.

The only method of **recognizing** with certainty whether a non-volatile solid is soluble in a liquid or not is to filter the mixture and evaporate a few drops of the filtrate on a clean watch-glass. For learning **how much** of the substance is contained in a given solution, a weighed quantity of the solution is evaporated to dryness and the weight of the residue determined. When the dissolved substance is volatile, its presence is often shown by some chemical test.

Ether and water is a case typical of the behavior of two liquids, each somewhat soluble in the other. After being shaken together, they seem to separate again completely into two layers (Fig. 84), with the ether uppermost. If, however, the water is withdrawn from beneath the ether, we find that, when heated, it gives off quantities of ether vapor which can be set on fire. Conversely, the addition of anhydrous cupric sulphate to a sample of the ether shows the presence of water in the latter, for the blue hydrated form of the substance is at once produced.

It must be stated explicitly that in going into *solution,* as we have used the term, a compound dissolves as a whole and, if the compound is pure (p. 8), any residue has the same chemical composition as the part which has dissolved. If the residue is a different substance, a chemical interaction with the solvent has occurred. If,

on evaporation, a different substance remains, there has also been chemical action.

The amount of the substance which has been dissolved by a given quantity of the solvent is described as the **concentration** of the solution. The *partial* removal of the solvent (as by evaporation) is called **concentrating,** its total removal **evaporating to dryness.** Note that a saturated solution need not also be a concentrated one. It will be very dilute, if the solute is but slightly soluble.

The term "strength" is too indefinite for scientific purposes. It may imply activity, or power of resistance, or pungency (in an odor), or, if it is used for solutions, it may be a measure of quantity. The amount of the substance which has been dissolved by a given quantity of the solvent is therefore described, in scientific work, as the **concentration,** rather than the strength of the solution. The terms "weak" and "strong" as applied to substances in solution have a connotation in chemistry entirely distinct from concentration, as will appear later (p. 295).

Units Used in Expressing Concentrations. — The concentrations of solutions, saturated and otherwise, are sometimes expressed in physical, and sometimes in chemical, units of weight. When **physical units** are employed, we give the number of grams of the solute held in solution by a fixed quantity, usually 100 grams or c.c. of the solvent.

When **chemical units** of weight are employed, two different plans are possible, and both are in use. Either the equivalent (p. 153) or the molecular weights may be taken as a basis of measurement. In the former case, the solutions are called **normal solutions,** and in the latter, **molar solutions.**

A normal solution contains one gram-equivalent of the solute in one liter of solution (*not* in 1 l. of solvent). The word "equivalent" has been used hitherto only of elements, and this application of the expression involves an extension of its meaning. **An equivalent weight of a compound is that amount of it which will interact with one equivalent of an element.** Thus, a formula-weight of hydrochloric acid HCl (36.468 g.) is also an equivalent weight, for it contains 1.008 g. of hydrogen, and this amount of hydrogen is displaceable by one equivalent weight of a metal. A formula-weight of sulphuric acid H_2SO_4 (98.076 g.), however, contains two equivalents of the compound, and a formula-weight of aluminium chloride $AlCl_3$ (133.35 g.) three equivalents. Hence normal solutions of these three substances contain, respectively, 36.468 g. HCl, 49.038 g. H_2SO_4, and 44.45 g. $AlCl_3$ per liter of solution. The special prop-

erty of normal solutions is, obviously, that equal volumes of two of them contain the exact proportions of the solutes which are required for complete interaction. Solutions of this kind are much used in quantitative analysis. We frequently use also decinormal or one-tenth normal solutions (0.1 N or $N/10$), seminormal solutions (0.5 N or $N/2$), six times normal solutions (6 N), and so forth.

A molar solution contains one mole (gram-molecular weight) of the solute in one liter of solution (*not* in 1 l. of solvent). When molecular formulæ (p. 188) are used, this means one gram-formula-weight per liter. In the cases cited above, the molar solution contains 36.468 g. HCl, 98.076 g. H_2SO_4, and 133.35 g. $AlCl_3$ per liter. As will be seen, the concentrations of molar and normal solutions are necessarily identical when the radicals are univalent.

Weight-normal and *weight-molar* solutions are occasionally employed in the study of certain physical properties of aqueous solutions (see pp. 216-7 below). These contain one gram-equivalent weight and one gram-molecular weight, respectively, of solute in 1000 *grams of water*.

Densities of Solutions. — The density or specific gravity of an aqueous solution is usually greater than that of water and, in each case, varies with the concentration. For commercial purposes, the concentrations of solutions are commonly defined by the specific gravity. Thus, we purchase ammonium hydroxide solution of "0.88 sp. gr.," containing 35 per cent of ammonia, or sulphuric acid of "1.84 sp. gr.," containing 94.8 per cent of the acid.

The commonly greater density of a solution is utilized in making solutions in chemical factories. Shaking several tons of the mixture is out of the question, and stirring costs money. If the solid is placed in the bottom of the tank, under water, a saturated solution is formed in the lowest layer of the water, and passage of the dissolving substance into the upper layers, by diffusion, would take months or years. Hence most of the solid would remain undissolved. But when the solid is placed on a *shelf* near the surface of the water, the solution sinks through the water, fresh water rises to the shelf, and a circulation is started. This results in the dissolving of the whole material in a surprisingly short time, with no expenditure of labor whatever.

Diffusion in Solution. — It was mentioned in the preceding paragraph that diffusion of a dissolved substance in aqueous solution

was an exceedingly slow process. Nevertheless, it is easy to show that, if we place a quantity of the pure solvent (Fig. 85) above a concentrated solution of a substance, and then set the arrangement aside, the dissolved body slowly makes its way through the liquid (Fig. 86), obliterating the original plane of separation. Eventually the dissolved body scatters itself uniformly through the whole. In other words, the molecules of the dissolved substance must be in rapid motion in the solution, although their rate of dispersion is much impeded by the close packing of the solvent molecules with which they are continually colliding.

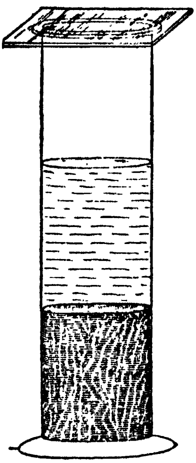


FIG. 85. Copper Sulphate Solution and Water (*before* Diffusion).

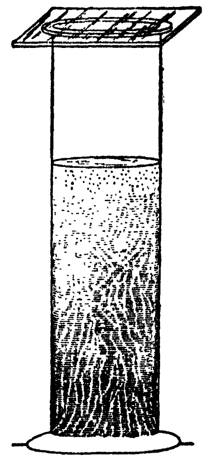


FIG. 86. Copper Sulphate Solution and Water (*after* Diffusion).

These solvent molecules are also in rapid motion in the solution, as we saw in the discussion of the properties of liquids in the light of the kinetic-molecular hypothesis (p. 168). A careful consideration of the ultimate structure of solutions shows, indeed, that the characteristics of solvent and solute molecules *while in the solution* are in no way different (as may best be seen by taking the case of a solution with two liquid components, such as alcohol and water), and we may therefore regard the molecules of a substance dissolved in a liquid as themselves also existent in the *liquid state.* This conception, we shall find, will be of considerable assistance to us in discussing other physical properties of solutions.

Is Dissolving a Physical or a Chemical Change? — This is a question still much debated amongst chemists (see p. 37). The general view is that in the most simple cases, like dissolving paraffin in gasoline or benzene, the process must be considered purely physical, and the solution contains *both* components in unchanged chemical condition.

This opinion is based upon the fact that, when the two components of the solution are mixed in the liquid state, there is no observable heat effect or

volume change on admixture, and the properties of the solution are all intermediate between those of the two pure substances, exactly as in the case of mixtures (p. 8). If one of the substances is added to the other as a solid or a gas, then the heat absorbed or evolved is practically identical with the heat required to melt the same quantity of the solid, or with the heat liberated in the condensation of the same quantity of the gas. Such solutions are called **ideal solutions** (see p. 213).

On the other hand, when water is used, as it is more frequently than any other solvent, chemical changes undoubtedly take place in addition. The water itself, at least, is always changed. Water *in the liquid state* is not simply H_2O. Its physical properties indicate that it is an *associated* liquid, extensive combination having taken place between simple H_2O molecules to form more complex molecules with the general formula $(H_2O)_n$. Dissolving *any* substance in water must upset the equilibrium (p. 169) between these different kinds of molecules:

$$(H_2O)_n \rightleftarrows nH_2O$$

and produce more of one and less of the other kind. This is the extent of the chemical change in the water alone.

The dissolved substance combines also, in the majority of cases, with part of the water. In a great many instances certain of the compounds formed can be definitely isolated from the solution, as, for example, in the case of hydrates such as $Na_2SO_4,10H_2O$ or $CuSO_4,5H_2O$. In other examples the exact nature of the compounds present in solution is often more difficult to determine, and no simple statement can as yet be made about them. But the compounds, whatever they are, are physically dissolved in the rest of the water and may be regarded as existent in the solution *in the liquid state,* just like any unchanged solute.

Dissolving, therefore, is generally partly a chemical, and only partly a pure physical process. The striking differences in solubility already mentioned (p. 199) may consequently be accounted for partly on a chemical, and partly on a physical basis. The main *chemical* factor is compound formation between the components of the solution. The more extensive this is, the greater, in general, is the solubility. Thus substances which form definite hydrates with water are mostly extremely soluble, while substances which are only difficultly soluble in water invariably crystallize out from an aqueous solution in an anhydrous state. The main *physical* factor is the relative magnitude of the cohesive forces between the various types of molecules present in the solution. Thus in the case

of water and benzene, the water molecules attract one another much more strongly than they do the benzene molecules. Molecules of benzene endeavoring to intermingle with water molecules encounter, therefore, very considerable resistance, and are almost certain to be squeezed out. The two liquids, indeed, are found to be practically immiscible.

Influence of Temperature on Solubility. — The quantity of a substance which will dissolve in a fixed amount of a given solvent depends very largely upon the temperature. Usually the solubility of solids in liquids increases with rise in temperature. Measurements may be made by the method described before (p. 200), using *excess* of the finely powdered solute with different portions of the same solvent in vessels kept at different temperatures. The most useful way of representing the results is to plot them graphically. The diagram (Fig. 87) shows the curves for a few familiar substances. The ordinates represent the number of grams of the anhydrous compound which is dissolved by 100 g. of water in each case. The abscissæ represent the temperatures. The concentration for any temperature can be read off at once. Thus, 100 g. of water dissolve 13 g. of potassium nitrate at 0° and 150 g. at 73°. The increase in solubility is here enormous. On the other hand, the same quantity of water will dissolve 35.6 g. of sodium chloride at 0° and 39 g. at 100°. The difference is shown at once when we examine the curves and observe that the line representing the solubility of sodium chloride scarcely rises at all between 0° and 100°, while that of potassium nitrate is extremely steep.

Cases in which the solubility of solids in liquids decreases with rise in temperature are less common. The solubility of slaked lime (calcium hydroxide $Ca(OH)_2$, used to make lime-water) is 0.175 g. at 20° and 0.078 g. at 100°. Anhydrous sodium sulphate Na_2SO_4 (p. 208) is another illustration of this type.

When two liquids are not completely miscible, their solubilities in each other are also found, in the majority of cases, to increase with rise of temperature. Thus 100 g. of water will dissolve only 8 g. of phenol (carbolic acid) at 10° and 100 g. of phenol will dissolve only 33 g. of water at the same temperature, but above 68.3° the two liquids are miscible *in all proportions*. In a few cases, however, the solubility increases with decrease of temperature. For example, 100 g. of water will dissolve only 5 g. of ether at 30°, but at 0° the solubility has risen to 13 g.

The solubility of gases in liquids *always* diminishes with rising temperature. This may be illustrated by heating cold tap-water in a beaker, when the dissolved gases, originally obtained from the air, are driven out in bubbles as the boiling-point is approached.

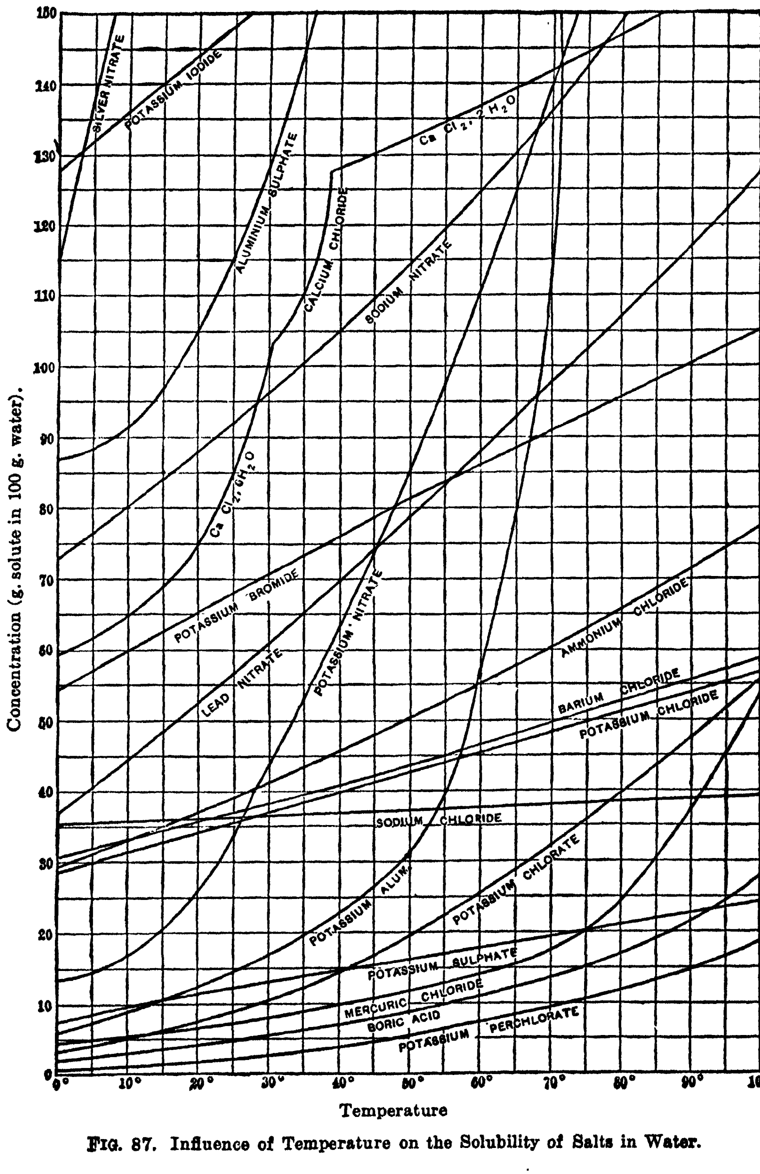


FIG. 87. Influence of Temperature on the Solubility of Salts in Water.

Crystallization. — If the solvent has been saturated while warm, and the dissolved substance is one that is less soluble at lower temperatures, then, when the temperature is allowed to fall and the merest trace of solute is introduced, the solute begins to come out of solution. The amount appearing, of course, is only the **excess** beyond what is needed to saturate the solvent at the lower temperature.

If the solute is a liquid, it appears at first as a cloud of drops, rendering the solution milky. This may be shown by cooling a solution of phenol in hot water. If the solute is solid, then the particles, as they appear, take the form of **crystals** (p. 59). These *grow* by taking on more of the separating solute. If the cooling goes on slowly, very large crystals can finally be obtained. On the other hand, with rapid cooling, new crystals are continually formed, and a fine crystal-meal falls to the bottom of the solution. The crystals in this meal, however, when viewed through a lens, are seen to be just as perfect as the larger ones.

Supersaturation. — When a hot, saturated solution is cooled in the *absence* of any undissolved solid, there is quite commonly some delay before the crystals begin to appear. The solution, pending the appearance of the crystals, is then said to be **supersaturated.** In most cases the crystals soon appear in due course, especially if the liquid is shaken or stirred. But certain substances have a tendency to remain indefinitely in the state of supersaturated solution. The hydrates of sodium sulphate (Glauber's salt $Na_2SO_4,10H_2O$) and of sodium thiosulphate (photographers' "hypo" $Na_2S_2O_3,5H_2O$) give solutions in water of this nature. The addition of a minute crystal of the substance concerned ("inoculation"), however, always starts the crystallization.

Many pure liquids, similarly, when cooled below their freezing-point, do not always crystallize out at once. Thus water can be taken down to — 10° without the appearance of ice. In this condition, it is said to be *supercooled.* Shaking, or stirring, or (better still) *inoculating* with a fragment of ice, induces crystallization in this case also. It may be noted that the opposite phenomenon has never been observed; ice invariably melts sharply at 0° under atmospheric pressure.

A very striking illustration of crystallization from a supersaturated solution may be obtained by saturating water with anhydrous sodium sulphate Na_2SO_4 at, say, 50°, at which temperature 100 g. of water take into solution 50 g. of Na_2SO_4 (Fig. 88). The excess of the solid is carefully and completely separated from the liquid, and

the latter is allowed to cool, say to 15°, in a flask loosely stoppered with cotton. The solution now contains a much smaller amount of sodium sulphate (Na_2SO_4) than at its present temperature it could acquire from contact with anhydrous sodium sulphate (62 g. at 15°, see dotted curve in the diagram). It is, therefore, impossible for the

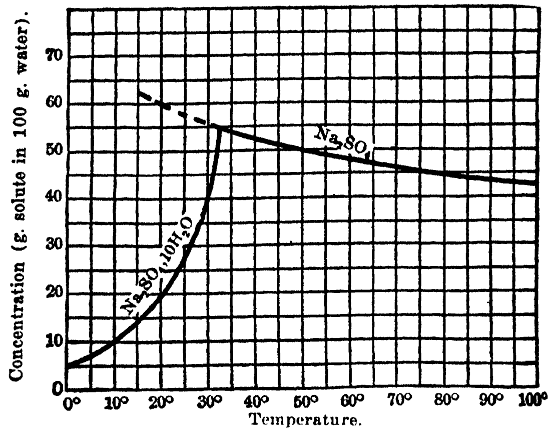


FIG. 88. Solubility Curves of Hydrated and Anhydrous Sodium Sulphate in Water.

solution to deposit crystals of this substance, with respect to which it is now unsaturated. On the other hand, it contains a much larger amount than it could acquire from contact with crystals of hydrated sodium sulphate $Na_2SO_4,10H_2O$ (13 g. at 15°). It is therefore highly supersaturated with respect to this substance. Yet in the absence of a crystal of the hydrated salt, no deposition of the dissolved substance begins. The solution may be kept indefinitely without alteration. The introduction, however, of the minutest fragment of the decahydrate at once starts the crystallization, the added crystal forming the center of a radiating mass of blade-like crystal clusters, which sprout with astonishing rapidity through the liquid (Fig. 89).

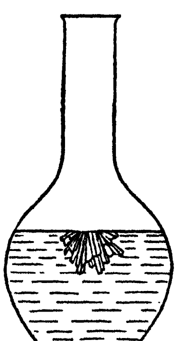


FIG. 89. Crystallization from a Supersaturated Solution.

Metastable Condition. — The above phenomenon is not an isolated or exceptional one in physical science It is frequently the case that, when the conditions for some physical change have been reached, the beginning of the physical change is delayed, sometimes indefinitely. The system is then said to be in a **metastable** condition.

It has already been mentioned that pure water may easily be cooled several degrees below 0° without the appearance of any ice. In like manner water may be heated to a temperature above 100° without boiling. Drops of water, suspended in some oil of almost the same specific gravity, may even be raised to 175° before the water turns into steam. This is because there is no water vapor (but only oil) in contact with the water. Similarly, air which is saturated with moisture, if it contains no dust, may be cooled without the appearance of fog.

Any system in the metastable condition may be transformed, however, to the stable condition merely by addition of the minutest trace of the more stable state, the appearance of which has been delayed.

Precipitation. — When two soluble substances are dissolved separately in water, and the solutions are mixed, chemical interaction frequently is evident between the dissolved materials. If one of the products is not very soluble, then a *supersaturated solution of this product may be thus produced.* As a rule, this substance immediately becomes visible as a fine powder, called a **precipitate,** suspended in the liquid (compare p. 31). More or less rapidly, according to its fineness of dispersion, this precipitate settles out, leaving the solution clear.

Often the precipitated product can be recognized by the physical *appearance* of the precipitate, and so this sort of action is used as a test for one of the *original* substances. Thus, precipitates are classified according to their color. Again, precipitates of the same color differ in degree of dispersion, and may be described as **gelatinous, curdy, pulverulent, or crystalline.** In the two former cases, at least, the precipitation is so sudden that there is not time for crystals to be formed, and the product is *amorphous* (see p. 62).

Phenomena of supersaturation, of a temporary kind at least, are extremely common in chemistry. Almost every delayed precipitation is a case of it. Barium sulphate, for example, is always slow in appearing in dilute solutions. So is sulphur, set free from dilute sodium thiosulphate solution by the action of an acid. In the latter case, instant re-neutralization with a base does not prevent the ultimate appearance of the sulphur, showing that the cause does not lie in slow interaction of the salt with the acid.

Heat of Solution. — The process of solution, in the case of most solid substances, *absorbs* heat, so that the solution becomes cooler as the crystals dissolve. Conversely the process of crystallization usually *evolves* heat. Thus, in the cases of $Na_2SO_4,10H_2O$ and $Na_2S_2O_3,5H_2O$ mentioned above, when the crystallization is brought about in the cool, supersaturated solutions, the rise in temperature is considerable.

This fact has been utilized in devising a sort of hot-water bottle. The bottle is made of rubber and contains a supersaturated solution of sodium acetate. Whenever the heat is wanted, the stopper is taken out, rubbed with the finger, and screwed back. The rubbing spreads on the inner surface of the stopper, next the liquid, some of the crystals adhering to the screw, and so starts the crystallization. The bottle then becomes warm and remains so for a considerable time. After it has cooled, it is placed, without being opened, in boiling water to redissolve the crystals, and, when cold, is ready for use again.

The solution of sulphuric acid in water is attended by an exceptionally large *evolution* of heat. One formula-weight of the pure acid, dissolving in a practically unlimited volume of water, liberates 39,170 calories. The solution of one formula-weight of sodium sulphate decahydrate in water, on the other hand, under the same conditions, *absorbs* 18,760 calories.

In both of the above cases, the magnitude of the heat effect varies considerably with the concentration of the solution. This is due to the fact that extensive chemical changes take place in the process of solution. With some salts in water (see cupric chloride, p. 286) the heat effect may even change in sign as the solution approaches saturation. Such solutions are evidently very far from *ideal*, since the heat absorbed in dissolving a formula-weight of a solid in an ideal solvent is identical with the molecular heat of fusion of the solid (p. 204), whatever the concentration of the solution.

The heat change involved in dissolving one formula-weight of a substance in a practically unlimited volume of its practically saturated solution is, we shall find in a later chapter (p. 284), a very important quantity. It is known as the **heat of solution.**

The Physical Properties of Solutions. — The physical properties of a solution depend, in all cases, upon its *concentration, i.e.*, upon the relative amounts of solvent and of solute present. The more concentrated the solution, the more will its physical properties, in general, differ from those of the pure solvent. The observed changes may be divided into two classes.

In the first class, the amount of the change varies with the substance dissolved. Very striking and difficult to explain, for example, are the erratic changes **in volume** which occur when solution takes place. Specific effects of this class show that chemical changes often accompany solution. For example, 58.5 g. of sodium chloride (volume 27.5 c.c.) and 10,000 c.c. of water have, separately, a vol-

ume totaling 10,027.5 c.c., but, when they are brought together, the solution measures only 10,016.5 c.c. This is a very dilute solution, so that the contraction of 11 c.c. is relatively considerable. On the other hand, 214 g. of ammonium chloride (volume 142.5 c.c.) and 843.5 c.c. of water have a total volume of 986 c.c., but when brought together give 1000 c.c. of solution. Here there is an expansion of 14 c.c. In the case of table-sugar and water, however, there is almost no change in volume.

The **heat effect in solution,** discussed in the preceding section and on p. 203, is similarly an irregular quantity, dependent entirely (for any given solvent) on the specific solute chosen. Another important property of solutions in which the influence of the solute is *specific* is **conduction of electricity.** Pure water is an exceedingly poor conductor. A solution of table-sugar in water is also practically non-conducting. But when acetic acid is dissolved in water a solution is obtained which conducts the current fairly well, while a solution of sodium chloride is an exceedingly good conductor. The significance of these differences in behavior will be taken up later (p. 294).

In the case of many properties of solutions, however, it has been found that, in a given quantity of solvent, *equal numbers of dissolved molecules of different substances produce the same amount of change.* The effect appears here to be due essentially to physical causes, and is discussed in the following sections in the light of the molecular hypothesis. Before attacking these sections, the student is recommended to refer back to pp. 169-70 and read those pages through again carefully, noting that the equilibrium relationships between liquid water and water vapor, therein discussed, can obviously be extended to any volatile substance in contact with its own vapor.

Vapor Tensions of Solutions. — When we take equal quantities of a volatile liquid (*e.g.*, benzene, C_6H_6) and add to each equal *weights* of different non-volatile solutes (*e.g.*, naphthalene, anthracene, camphor; three organic solids which are relatively non-volatile at ordinary temperatures) we find that the vapor tensions of all the resulting solutions are less than that of the pure solvent, but the depression is different in each case. But if, instead of adding equal *weights* of the different solutes, we add *equal numbers of molecules* (as we can do by dissolving, for example, 1 g. molecular weight of each substance in 1000 g. of benzene), we find that *the depression is the same in every case. The depression is proportional,*

moreover, to the fraction of solute molecules in the solution (**Raoult's law**). This very striking fact is explained by the molecular hypothesis as follows:

Every molecule at the surface of a pure volatile liquid has an equal chance to escape into the vapor above the liquid. But as soon as we add to such a liquid a solute which is practically non-volatile, we have a liquid in which some of the molecules have no tendency to pass into the state of vapor, but are *fixed* in the liquid state. Suppose, for instance, we consider a solution in which one molecule in every ten is non-volatile; the intensity of the hail of molecules leaving the liquid will evidently be reduced by one-tenth. Equilibrium between liquid and vapor over such a solution will be re-established only when the intensity of the hail of vapor molecules returning to the liquid is also reduced by one-tenth, since otherwise more molecules will be returning than leaving. This means that the vapor tension of the solution must be one-tenth less than that of the pure solvent.

It is important to note that the *nature* of the solute is here immaterial, the essential factor is the number of molecules it furnishes to the solution. We have here a method of determining *the molecular weights of non-volatile substances*. By dissolving a known weight of such a substance in a known weight of a suitable solvent and determining the *relative depression of vapor pressure* thereby produced, we learn what fraction of the molecules in the solution belong to the solute, and hence can calculate its molecular weight.

All aqueous solutions show a lower tension of water vapor than does pure water. With *conducting* solutes (*e.g.*, sodium chloride), indeed, the vapor pressure depressions obtained are abnormally large, and do not agree with the accepted molecular weights. This is a point to which we shall return later (p. 295).

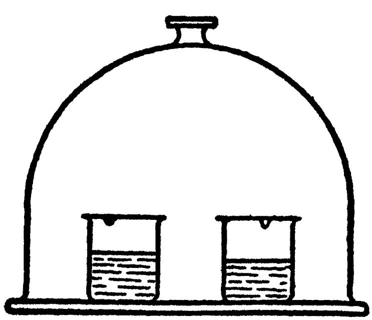


Fig. 90.

If a substance is very soluble in water, the solution may give a vapor tension of water less even than that commonly present in the atmosphere. Such a solution, placed in an open vessel, will not evaporate. On the contrary, it will take up moisture from the air and increase in bulk. For this reason very solu-

ble substances are commonly moist and, when exposed to the air, extract water from the latter and dissolve in this water. This behavior is called **deliquescence,** and is shown, for example, by the hydrate of calcium chloride $CaCl_2, 6H_2O$, used to dry gases (pp. 138, 157).

The principle involved will become clear if we imagine two vessels, one containing pure water and one an aqueous solution, to be placed on a glass plate and covered by a bell jar (Fig. 90). Each liquid exchanges water molecules with the moist air in the jar, but the solution gives off water more feebly than does the pure water. The result is that the latter can produce a pressure of water vapor higher than that which would be in equilibrium with the solution. The solution, therefore, receives continuously more molecules than it emits, and increases in volume. The pure water thus gradually passes through the vapor state into the solution until it is all gone. If sufficient water was present, the process would go on until the solution became infinitely dilute.

Ideal Solutions. — The conception of an **ideal solution** (p. 204) is one which it is essential for the student to grasp properly. The simplest case of an ideal solution is expressed by *Dalton's law of partial pressures* (p. 116). The two components of the solution are here in the gaseous state. Each behaves just as if the other were absent and the pressure exercised by each is proportional to its concentration.

Ideal liquid mixtures behave in exactly the same way. The two components do not affect each other's properties at all, except in so far as molecular concentrations are varied. Take, for example, a cylinder half-filled with a mixture of **benzene** and **toluene** (two liquid hydrocarbons, see p. 587) in equal molecular proportions. The presence of the toluene molecules does not affect the behavior of the benzene molecules, either in the liquid or the vapor state. Neither does the toluene act any differently from what it would in private. But there is one very important result of the fact that only 50 per cent of the molecules in the liquid state belong to each species: *The number of benzene molecules escaping into the vapor per second is only one-half of what it would be if the liquid were pure benzene.* Similarly the number of toluene molecules escaping into the vapor per second is only one-half of what it would be if the liquid were pure toluene. Evidently equilibrium between the liquid and vapor states will be established only when the respective vapor concentrations are correspondingly reduced to one-half. That is, the partial vapor pressure of benzene above the solution will be one-half that of pure benzene; the partial vapor pressure of toluene above the solution will be one-half that of pure toluene. More

generally, the partial vapor pressure of any component of an ideal solution is proportional to the molecular fraction, x, of that component in the solution. This is the most general form of statement of **Raoult's law.** It is expressed graphically in Fig. 91.

When only one of the components of a solution is volatile at ordinary temperatures, then the law may be stated somewhat more simply (p. 212). **The vapor pressure lowering of a volatile solvent on addition of a non-volatile solute is proportional to the fraction of solute molecules in the solution.**

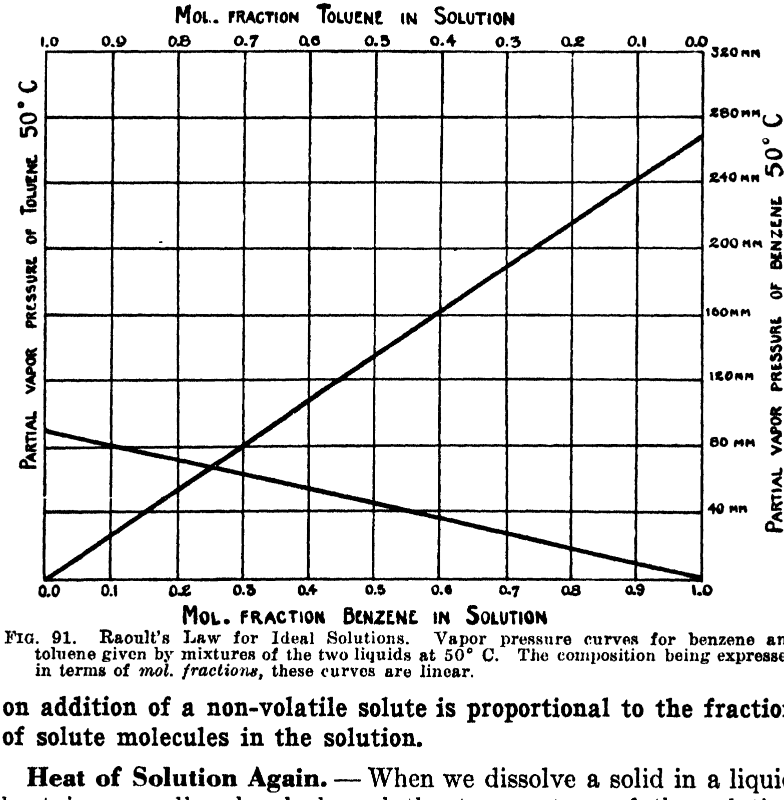


FIG. 91. Raoult's Law for Ideal Solutions. Vapor pressure curves for benzene and toluene given by mixtures of the two liquids at 50° C. The composition being expressed in terms of *mol. fractions*, these curves are linear.

Heat of Solution Again. — When we dissolve a solid in a liquid heat is generally absorbed, and the temperature of the solution falls. When we dissolve a gas in a liquid heat is *always* evolved. The resultant solution, in either case, behaves *ideally* (follows Raoult's law, for example) only if the *heat of solution* is identical with the heat involved in the change of physical state, *i.e.*, with the heat of fusion or the heat of condensation respectively. **We must therefore regard both components of an ideal liquid mixture as existent in the liquid state in the solution, whatever their original**

condition. It is important to emphasize this, since many chemists still cling to an old idea that the solute in a dilute solution must be considered as existent in the *gaseous* state. This conception has now been definitely abandoned (p. 610).

Non-Ideal Solutions. — In very many cases, chemical reactions undoubtedly occur in the process of solution. The heat of solution will of course be affected by the heat changes accompanying such reactions. The formation of new molecular species will make all of our calculated molecular fractions erroneous, and exact agreement with Raoult's law cannot be expected. Nevertheless, we find that this law does apply quite satisfactorily for certain non-ideal solutions so long as one component is present in very great excess. The molecular weight of a substance such as *sugar*, for example, may be determined with a high degree of accuracy by measuring the vapor-pressure depression of a dilute aqueous solution, even although we know that this solution is not strictly ideal (p. 204). Methods based upon two other properties which are intimately connected with vapor-pressure lowering — *boiling-point elevation* and *freezing-point depression* (see next two sections) — are usually employed instead in actual practice, but merely because of greater experimental convenience.

Elevation in the Boiling-Point of a Solution. — A solute lowers the vapor tension of a solvent, not only at room temperature, but at all temperatures. Thus, at 100°, a 7.5 per cent solution of potassium chloride shows a vapor tension of only 734.1 mm., while that of water is 760 mm. The lowering is 25.9 mm. Hence, **the solution has to be raised to a higher temperature** (100.96°) **before it boils.**

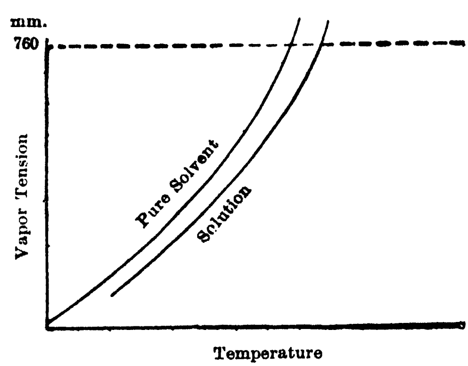


Fig. 92. Elevation of Boiling-Point.

This conclusion may also be reached graphically (Fig. 92). The ordinates represent the vapor tensions corresponding to the temperatures shown by the abscissæ. The horizontal dotted line shows the vapor tension of 760 mm., at which any liquid will boil under standard atmospheric pressure. The boiling-point of the solvent is therefore the tem-

perature at which its curve intersects this line. Since the vapor tension of the solution at any temperature is less than that of the solvent, its curve lies below that for the solvent, but ascends along with the latter. Hence, it also cuts the 760 mm. line, but at a point *beyond* the boiling-point of the pure solvent. Since, for short lengths, the curves are very nearly straight lines, the distances from boiling-point to boiling-point for a series of dilute solutions are very nearly proportional to the vertical distances between the curves. That is to say, the **elevations in the boiling-point, for dilute solutions, are proportional** to the depressions in the vapor tension, and therefore **to the fraction of involatile solute molecules in the solution.**

When **different substances** in the **same solvent** are compared, **equal molecular concentrations of the solutes give equal elevations in the boiling-point.** Thus, 1 gram-molécular weight of sugar (342 g.), or of glycerine (92 g.), dissolved in 1000 g. of water, will elevate the boiling-point from 100° to 100.52° (polar solutes behave abnormally, see Chap. XVII). When the effects of the same solute **in different solvents** are compared, the scale of the elevation alone is different.

Molecular weights of non-volatile, non-conducting substances can therefore be determined by finding out what weight of the substance, when dissolved in 1000 g., is required to raise the boiling-point of water from 100° to 100.52°.

Freezing-Points of Solutions: Freezing Mixtures. — Every pure liquid has a definite temperature at which it freezes. Thus, pure water freezes at 0° and benzene at 5.5°. The freezing of a dilute solution consists, usually, in the crystallization of some of the *pure solvent* only. The presence of a foreign, dissolved body tends to prevent this freezing, and so solutions can be frozen only at temperatures below the freezing-point of the pure solvent. Thus, sea-water is harder to freeze than fresh water. **The freezing-points of dilute solutions are found to be depressed below that of the solvent in proportion to the molecular fraction of the solute** * (again, polar solutes behave abnormally, see Chap. XVII).

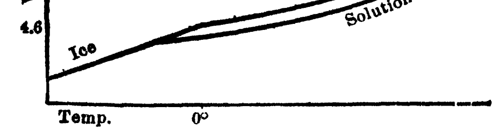


FIG. 93. Depression of Freezing-Point.

* Only when the solid which separates consists of the pure solvent, and the solute does not enter into it, does this law represent the facts.

This may also be shown graphically (Fig. 93). The ordinates represent vapor tensions corresponding to the temperatures shown by the abscissæ. In the region of the freezing-point, the rate at which the tension rises is greater for ice than for water, hence the ice curve is steeper. At 0°, ice and water can coexist permanently (p. 162). By measurement, they have the same vapor tension (4.6 mm.) at this point. Theoretically, if they had not, they could not coexist indefinitely, for the one with the greater vapor tension would evaporate, and its vapor would condense on the other, until one of them alone remained.

Now the vapor tension of a solution is, at all temperatures, lower (Fig. 93) than that of water. Hence, for a solution, the curve must cut the ice curve below 4.6 mm. and therefore behind 0°. In other words, ice and the solution cannot have equal vapor tensions, and therefore coexist indefinitely, except at some temperature below 0°. But the temperature at which ice can exist indefinitely in a solution is the freezing-point. Hence, freezing-points of solutions are always lower than those of the pure solvents.

By measuring the vapor tensions of the solution at several temperatures, in order to see how far the curve for the solution is below that of water, and then producing the curve for the solution backwards, the intersection with the ice curve, and therefore the freezing-point, may be obtained graphically. Direct measurement always confirms the result.

Since the ice curve is, for a short distance, almost a straight line, it follows that the depressions of the freezing-point are proportional to those of the vapor tension, and these in turn are proportional to the molecular concentrations.

Equal numbers of molecules of different solutes in the same quantity of solvent, consequently, give equal depressions of the freezing-point. Numerically, in the case of water, one molecular weight of a substance such as sugar (342 g.) or glycerine (92 g.), dissolved in 1000 g. of water, will cause the water to begin to freeze at —1.86° instead of 0°. Molecular weights can thus be measured by this method also.

This fact likewise explains why salt, thrown on ice, causes the latter to melt. A saturated solution of salt does not freeze until cooled to —21° C. (—6° F.), and it then gives a fine *mixture* of pure ice and pure $NaCl,2H_2O$, misnamed a **cryohydrate.** Hence, ice and salt cannot permanently exist together *above* that temperature. When the outside temperature is below — 21°, salt will no longer melt the ice. But calcium chloride, which is more soluble, will do so. **A mixture of ice and salt, giving the temperature —21°, is called a freezing mixture.** Such a mixture is used in freezing ice cream and ices.

Definition of a Saturated Solution: A Warning.—To avoid a common **misconception,** it must be noted that solution is *not* a process of filling the pores of the liquid. If that were true, approximately equal weights of all substances would find accommodation in equal volumes of water. The fact is that, for example, 100 c.c. of water will dissolve 195 g. of silver fluoride, but only 0.00000035 g.

of silver iodide, although the space available (if there *is* any such space) is the same in both cases.

The same conclusion is reached when we consider that a simple salt and its various hydrates all have *different* solubilities, although the solutions which they give in water are identical. Thus, at 20°, the addition of excess $Na_2SO_4,10H_2O$ to water will give a solution containing about 18 g. of Na_2SO_4 to 100 c.c. of water. But excess of *anhydrous* sodium sulphate Na_2SO_4 at 20° gives a solution containing 59 g. to the same amount of water. The phrase, "a saturated solution of sodium sulphate," is therefore devoid of definite meaning. We must describe the liquid as a solution saturated by anhydrous, or by hydrated sodium sulphate, as the case may be.

The reader is also warned against the frequent definition of a *saturated solution* as one containing all of the solute that it *can hold*. A supersaturated solution evidently holds more. The saturated solution under any given conditions is *that solution which, when placed in contact with excess of the solute, is found to be in equilibrium.*

The molecular hypothesis may again be called to our assistance in this connection. When we have a solute (either crystalline, or liquid, or gaseous) in contact with its saturated solution, and therefore in equilibrium with it, two opposing tendencies must balance each other at the surface of contact. One of these is the tendency of the solute particles to escape into solution, the other is the tendency of the solute particles already in solution to return back to the solute. The first of these tendencies (the intensity of the hail of particles thrown off from the surface of the solute into a given solvent, under given conditions of temperature and pressure) we may regard as constant. The second tendency (the intensity of the hail of particles returning from the solution to the surface of the solute) will increase steadily as the concentration of the solute particles in the solution increases. At one definite concentration only, therefore, can these two opposing tendencies counterbalance, namely that of the *saturated solution.* The rate at which solute particles are returning from the solution just equals, in this case, the rate at which they are entering. With *unsaturated* solutions, containing *less* solute, the number of returning particles will be deficient, and the solute will continue to dissolve until it all disappears or saturation is reached. With *supersaturated* solutions, on the other hand, containing *more* solute, the number returning will be in excess, and deposition of home-coming particles on the solute surface will continue until this excess is wiped out.

If, however, we have a supersaturated solution in which no free solute is present, the solute particles in the solution have no home to return to, no surface upon which they can deposit themselves. They are therefore compelled to continue wandering around and around in the solution, having lost their equilibrium completely. By violent shaking or stirring we may succeed in inducing crystallization in such a solution, but the only certain means of establishing equilibrium conditions is inoculation with a small fragment of the solute.

Conditions Affecting the Solubility of a Gas. — When the dissolving substance is a **gas,** led through or confined above the liquid at a definite pressure, the gas dissolves until a state of equilibrium between dissolving and emission is reached, for example, Oxygen (gas) $\rightleftarrows$ Oxygen (dissolved), and the liquid is then saturated with the gas.

It is found, as the molecular theory would lead us to expect, that **the concentration of the saturated solution of a gas is proportional to the pressure at which the gas is supplied (Henry's law).** Henry's law is clearly only a particular case of Raoult's law, as developed in detail for ideal solutions above (p. 213).

This equilibrium, Gas (gaseous) $\rightleftarrows$ Gas (dissolved), can be reached, naturally, from the other direction, namely by starting with a solution of the gas and a space above the solution containing, at first, none of the gas. The gas leaves the solution until the rates of emission and return become equal. Hence, a gas may be entirely removed from solution by bubbling a foreign gas through the liquid. The bubbles furnish the space to receive the emitted gas, and have a large surface, so that the process goes on rapidly. The bubbles also escape, and carry with them the emitted gas, so that, in this case, there is no re-solution. This is a case of nullifying one of the two opposed tendencies (p. 177).

The solubilities of *different* gases, even when their pressures are equal, vary enormously. One volume of water will dissolve 1300 volumes of ammonia at 0° and 760 mm., while it will dissolve only about 0.02 volumes of hydrogen under the same conditions. In one volume of alcohol, at 0° and 760 mm., 17.9 volumes of hydrogen sulphide or 0.07 volumes of hydrogen may be dissolved. Henry's law describes the behavior of any one gas in non-ideal solutions with exactness only when low gaseous pressures, or gases whose solubility is small, are in question. Great solubility must be due, in general, either to chemical union between a part, at least, of the gas and the solvent, or to cohesive influences which the molecules exert upon one another. The law, and

the kinetic-molecular explanation of the law, on the other hand, consider only an ideal behavior involving complete independence of the molecules.

When **a mixture of two gases** is in contact with the solvent, the molecular viewpoint enables us successfully to foretell what will happen. The quantity of each gas which can remain dissolved must depend simply upon the frequency with which *its own* molecules strike the liquid, and must be independent of the presence of the other gas. Hence the solubility of each gas is the same as if it were present alone at its own partial pressure (Dalton's law, p. 116). In other words, each gas has the same pressure, and therefore the same solubility, as it would possess if it alone occupied the *whole* space above the liquid.

Air dissolving in water is an illustration of this principle. It does not dissolve as a whole, but the oxygen and nitrogen dissolve each in proportion to its intrinsic solubility and partial pressure.

Two Immiscible Solvents: Law of Partition. — An interesting application of the same ideas may be made to a case which occurs very commonly in chemical work. If we shake up a small particle of iodine with water, we find that it dissolves slowly, giving eventually a saturated but very dilute solution. In ether, however, iodine is much more soluble. If, now, ether in sufficient quantity be shaken with the aqueous solution, the greater part of the iodine will find its way into the ether, and be contained in the brown layer which rises to the top. The process of removing a substance practically from solution in one solvent and securing it in another is called **extraction.** We find in such cases that neither solvent can entirely deprive the other of the whole of the dissolved substance. A state of equilibrium is finally reached: I_2 (in water) $\rightleftarrows$ I_2 (in ether). The partition of the substance takes place in proportion to its solubility in each solvent **(law of partition).** It is found that any amount of the solute, up to the maximum the system can contain, provided the solute exists in the same molecular state in either solvent, is divided so that the ratio of the concentrations in the two solvents is always the same. In the case of iodine divided between water and ether, this distribution ratio at 18° is approximately 1 : 200.

This principle is used in Parke's process for extracting silver from molten lead, by means of molten zinc as the second solvent. It is employed in separating interesting compounds from animal secretions and vegetable extracts, and in purifying such compounds. Nicotine from tobacco and cocaine from coca leaves are secured in this way.

The aqueous solution of potassium iodide has a very great power of dissolving iodine, and we find that in the presence of this salt the ether leaves a

much larger share of the element in the lower layer. A part of the iodine combines to form KI_3, however, so that this is not a case of simple solution, and the law of partition does not hold. The chemical equilibrium (see Chap. XVI) between free and combined iodine in the aqueous layer has to be considered.

Exercises. — 1. Give other examples of limited solubility in various solvents (p. 199).

2. What weights of phosphoric acid (p. 148) and of sodium hydroxide, respectively, are required to make 1 liter of a normal solution?

3. Express the concentrations of solutions of ammonium chloride, saturated at 0° (sp. gr. 1.076), and of potassium sulphate K_2SO_4, saturated at 10° (sp. gr. 1.083), in terms of a normal solution (pp. 201, 206).

4. Express the concentration of a five per cent aqueous solution of phosphoric acid (sp. gr. 1.027), in terms of a normal and a molar solution, respectively.

5. Explain why, (*a*) pulverization and, (*b*) agitation hasten the dissolving of a solid.

6. Read from the curves (p. 206) the solubilities of potassium nitrate at 15°, of potassium chloride at 30°, of potassium chlorate at 45°. What are the relative rates at which the solubilities of these salts increase with rise in temperature?

7. At what point in a tank of water should you introduce ammonia gas, in order, with the least effort, to saturate the water? The sp. gr. of the saturated solution is 0.88.

8. Give two ways of separating a mixture, consisting of a suspended solid and a liquid (p. 198).

9. If you had a spot on your clothing consisting of: (*a*) grease, (*b*) sugar, or (*c*) sugar and grease together, or (*d*) varnish, how should you proceed in each case to remove the spot?

10. If chalk (5 g.) and potassium chlorate (5 g.) were mixed, how should you separate them (p. 21)? Explain how you could secure each substance.

11. Could you make (*a*) a concentrated, (*b*) a saturated solution of chalk in water (p. 199)? Of alcohol in water?

12. If you saturated 200 g. of water at 70° with (*a*) salt, or (*b*) potassium nitrate, and then cooled the clear liquid to 20°, what weight of the solid substance would separate out in each case (p. 206)?

13. To make as concentrated a solution of lime-water as possible, should you use hot water or cold (p. 205)?

14. Explain why boiled water has a slightly different taste from tap-water that has not been boiled (p. 205).

15. If 100 g. of a non-volatile substance, dissolved in 1000 g. of benzene (C_6H_6), lower the vapor pressure from 74.8 to 68.0 mm., what is the molecular weight of the substance? (Use Raoult's Law, p. 212.)

16. Explain why potassium carbonate becomes wet, and finally dissolves, when exposed to moist air. How must calcium chloride be preserved from becoming moist?

17. If 52 g. of a substance dissolved in 1000 g. of water gives a solution boiling at 100.26°, what is the molecular weight of the substance (p. 216)?

18. If 68.5 g. of a substance dissolved in 500 g. of water gives a solution freezing at —1.86°, what is the molecular weight of the substance (p. 217)?

19. Explain why a sodium acetate hot-water bottle can be used over and over again. What is the source of the heat it gives out each time it is used?

20. If you were not permitted to evaporate sea-water to dryness, how should you show that it was a solution and not a pure substance?

21. Reëxpress Henry's law (p. 219) in terms of the volume of gas dissolved at different pressures.

22. When a solution of a very soluble substance, like zinc chloride, is evaporated to dryness on a water bath, why is the escape of the last portions of the solvent so much slower than is that of the first?

23. In order to make up 500 c.c. of a decinormal solution, how much of each of the following substances would you need to weigh out: (*a*) NaCl; (*b*) Na_2SO_4; (*c*) $Na_2SO_4,10H_2O$; (*d*) $Al_2(SO_4)_3,18H_2O$?

24. A saturated solution of thallous chloride TlCl in water at 18° contains 0.304 g. per liter. A saturated solution of thallous bromide TlBr contains 0.042 g. per liter. A saturated solution of thallous iodide TlI contains 0.056 g. per liter. Convert these values into normalities (p. 201).

25. The molar solubility of silver iodide in water at 25° is 1.5×10^{-8}. Convert this first to g. per liter. Calculate next how many atoms of silver are present in 1 c.c. of the saturated solution. Is silver iodide "insoluble" in water?

26. What is the concentration, in terms of a normal solution, of a saturated solution of calcium hydroxide (*a*) at 20°, (*b*) at 100°? (p. 205, disregard density deviations from unity.) 200 c.c. of a solution saturated at 20° are raised to 100° and filtered. What weight of solid is retained by the filter?

27. What weight of anhydrous sodium sulphate must be added to 500 g. of water at 75° to obtain a saturated solution (p. 208)? If the solution is cooled to 10°, and a minute crystal of the decahydrate added, what weight of the salt will still remain in solution? What weight of the decahydrate will crystallize out?

28. Prove, in connection with Fig. 91, that the *total* vapor pressure above any solution is expressed by the straight line joining the vapor pressures of the two pure components.

29. Two barometer tubes are set up. Into the vacuum above the mercury in one a few c.c. of ether are introduced. Into the second a few c.c. of a concentrated solution of naphthalene (p. 211) in ether are introduced. What do you observe? Explain.

30. Calculate the vapor pressure depression when 100 g. of diphenyl $C_{12}H_{10}$ are dissolved in 1000 g. of benzene C_6H_6 at 20°. The vapor pressure of pure benzene at 20° is 74.8 mm., diphenyl is practically non-volatile at 20°, and the solution is ideal.

31. Explain why only those substances which are very soluble in water deliquesce when exposed to the air under ordinary conditions.

32. Show that if the air is practically *saturated* with water vapor (as it is on a damp, foggy day) even slightly soluble substances will begin to deliquesce.

33. In 1840, Dalton announced that he had discovered that salts have no volume in solution up to the point of saturation. "The salt," he claimed, "enters into the *pores* of the water. The water and solid matter are the *same in bulk* as the water itself. This fact was new to me and, I suppose, to others. *It is the greatest discovery that I know of, next to the atomic theory.*" — What have you learned in this chapter that leads you to conclude that Dalton was (*a*) a very crude experimenter, and (*b*) not invariably right in his deductions?

34. From the following data, plot the solubility curves of calcium chromate and its various hydrates in water. Solubilities are expressed in grams solute per 100 g. water, as on p. 206.

T. (° C.)	0	18	30	50	75	100
$CaCrO_4$	4.5	2.32	1.96	1.12	0.75	0.42
$CaCrO_4$, $\frac{1}{2}H_2O$	7.3	4.8	3.9	1.63	1.05	0.81
$CaCrO_4$, H_2O	13.0	10.6	9.5	7.2	4.8	3.2
$CaCrO_4$, $2H_2O$ (rhombic)	10.9	11.5	11.6	....	....	....
$CaCrO_4$, $2H_2O$ (monoclinic)	17.3	16.7	16.5	....	....	....

Discuss briefly the significance of the curves.

35. The following table shows the solubility figures for the system phenol-water (p. 205):

T. (° C.)		10	20	30	40	50	60	65	68.3
G. phenol per 100 g.	Aqueous layer	7.5	8.3	8.8	9.6	12.0	16.7	21.9	33.4
	Phenol layer	75	72.1	69.8	66.9	62.7	55.4	49.2	33.4

Plot *temperature* against *g. phenol in* 100 *g. solution,* and fill in the curve.

36. Mixtures of propylene bromide $C_3H_6Br_2$ and ethylene bromide $C_2H_4Br_2$ at 85° show the following vapor pressures of each component:

Mol. fraction $C_2H_4Br_2$ in mixture	0	0.2	0.4	0.6	0.8	1.0
Partial pressure $C_2H_4Br_2$ in mm.	0	34.4	69.0	102.5	147.8	172.6
Partial pressure $C_3H_6Br_2$ in mm.	128.0	102.8	76.0	50.9	25.6	0

Plot the partial pressure curves for the two components and also the total vapor pressure curve of the mixture. Are the solutions ideal?

37. The freezing point depressions obtained on addition of mannite to water are as follows:

G. mannite to 1000 g. water	4.095	9.178	21.80	49.33	99.43
Freezing pt. depression, ° C.	0.0417	0.0931	0.2225	0.505	1.019

Plot the curve and extend it to —1.86°. What is the molecular weight (approximate) of mannite? Given that its percentage composition is carbon 39.55, hydrogen 7.75, oxygen 52.70; derive its molecular formula.

38. The boiling point elevations obtained on addition of glucose (p. 191) to water are as follows:

G. glucose to 1000 g. water	41.4	92.0	193.0
Boiling pt. elevation, ° C.	0.122	0.270	0.573

Plot the curve and determine from it the approximate molecular weight of glucose. Given that its percentage composition is carbon 39.98, hydrogen 6.72, oxygen 53.30; derive its molecular formula.

READING REFERENCE

Rohrman and Taylor; The Preparation of Large Crystals of Chrome-Alum. Journal of Chemical Education, 6, 473, 1929.

CHAPTER XIII

HYDROGEN CHLORIDE AND SODIUM HYDROXIDE

We have had occasion several times to mention common salt, or sodium chloride NaCl. This is one of the most familiar chemical substances. Large quantities of it are used in the household, in cooking and in making freezing mixtures. Still larger amounts are consumed in manufacturing washing soda, caustic soda, and soap, for all of which it furnishes the necessary sodium. It is used also in preserving fish and other foods. It supplies the chlorine used in bleaching and in the sterilization of city waters. We shall consider it first as a means of making hydrogen chloride and sodium hydroxide, and shall take the opportunity in this chapter to develop the properties of these two very important substances in some detail.

Preparation of Hydrogen Chloride HCl from Salt. — When a few drops of concentrated sulphuric acid (H_2SO_4) are poured upon common salt in an open dish, vigorous effervescence begins. This indicates that a gas is forming in bubbles in that part of the liquid which is immediately in contact with the salt and that the bubbles are rising through the upper layer of acid and bursting at the surface. The gas is itself invisible, but when we breathe upon the contents of the vessel, a heavy fog is produced. This is due to condensation of water vapor (in the breath) to droplets of water, in which the gas has dissolved. The fog is composed, in fact, of drops of a solution of hydrogen chloride (HCl) in water, which receives the name of **hydrochloric acid** (in commerce, muriatic acid, from the Latin *muria,* brine). Other very soluble gases (pp. 348, 421) give similar fogs with water vapor.

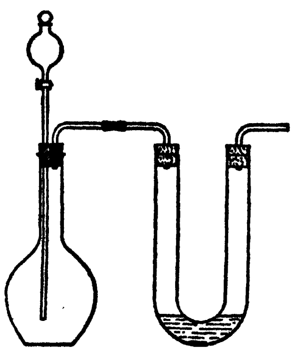


FIG. 94. Preparation of Hydrogen Chloride.

In order to handle the gas more readily, the sulphuric acid may be allowed to fall from a funnel, drop by drop, upon salt con-

tained in a flask (Fig. 94). Soon the air in the flask is all displaced by the gas, and the latter issues from the open delivery tube. If a **U**-tube containing some water is attached to the delivery tube, the gas dissolves in the water as fast as it is formed.

If the correct proportions of the materials are used, then, when the action is over, all that remains in the flask is a white solid, different from salt, and called sodium-hydrogen sulphate $NaHSO_4$. The equation is easy to make from the formulæ given,

$$NaCl + H_2SO_4 \rightarrow HCl \uparrow + NaHSO_4, \qquad (1)$$

and requires no further balancing. (An arrow pointing upward is used in equations to indicate that the substance to which it refers removes itself effectively from the reaction by escaping in the form of a gas.)

The action described is the one which occurs in the laboratory. When a double proportion of salt and a high temperature are used, a second action occurs:

$$NaCl + NaHSO_4 \rightarrow Na_2SO_4 + HCl \uparrow$$

and sodium sulphate Na_2SO_4 remains. In Europe this action is employed, with furnace heat, in manufacturing sodium sulphate, from which sodium carbonate is afterwards prepared. The hydrogen chloride passes into a tower, down which water trickles over lumps of coke, and is dissolved.

Analysis of the Interaction of Sulphuric Acid and Salt.— One who has used the above described method for making hydrogen chloride without reflection would not realize the complexity of the machinery by which the result is achieved. The means are apparently very simple. Yet the mechanical features of this experiment, when laid bare, are extremely curious and interesting. A single fact will show the possibilities which are concealed in it.

If we take a saturated solution of sodium-hydrogen sulphate in water and add to it a concentrated solution of hydrogen chloride in water (concentrated hydrochloric acid), we shall perceive at once the formation of a copious precipitate. This is composed entirely of minute cubes of sodium chloride:

$$NaHSO_4 + HCl \rightarrow H_2SO_4 + NaCl \downarrow. \qquad (2)$$

(An arrow pointing downwards is used in equations to indicate that the substance to which it refers removes itself from the reaction in the form of a precipitate.) Now this action is nothing less than the precise reverse of (1), yet it proceeds with equal

success. In fact, this chemical interaction is not only **reversible** (p. 173), but can be carried virtually to completion in *either* direction. It is only in presence of a very large excess of water, sufficient to keep all of the substances involved in solution, that it is valueless for securing any practical transformation.

In equation (1) the salt dissolved to some extent in the sulphuric acid, and so, by intimate contact of and interaction of solvent and solute in the resulting solution, the products HCl and $NaHSO_4$ were given the opportunity to form. On the other hand, the hydrogen chloride, being practically insoluble in sulphuric acid, escaped as fast as it was formed: HCl (dslvd.) $\rightarrow$ HCl (gas). Hence, in that case, almost no reverse action was possible, and consequently the passage of salt into solution and the subsequent double decomposition (p. 230) went on virtually to completion. With all the sodium-hydrogen sulphate in the bottom of the flask, and most of the hydrogen chloride in the space above, the two products might as well have been in separate vessels so far as any efficient re-interaction was concerned. This plan, in which water is purposely excluded, forms therefore the method of making hydrogen chloride.

In equation (2), on the other hand, the hydrogen chloride was taken *in aqueous solution*, and was mixed with a concentrated solution of sodium-hydrogen sulphate. The acid was, therefore, kept permanently in full contact with the sodium-hydrogen sulphate. It had, in this case, every opportunity to interact with the latter and no chance of escape. Furthermore, sodium chloride, one of the products formed by such interaction, is not very soluble in concentrated hydrochloric acid (far less so than in water), and so it came out as a precipitate. But this was almost the same as if it had gone off as a gas. It meant that the greater part of the salt was in the solid form. In this form, it was no longer able to interact effectively with the other product, the sulphuric acid. Hence, there was little reverse action to impede the progress of the primary one. Thus (2) is nearly as perfect a way of liberating sulphuric acid as (1) is of liberating hydrogen chloride.

Other Sources of Hydrogen Chloride. — Chlorides of other metals could be substituted for the sodium chloride in action (1), and all but the less soluble ones would give hydrogen chloride freely. Common salt is employed because it is the cheapest of the chlorides.

While theoretically any acid would, like sulphuric acid, furnish the required hydrogen, and liberate hydrogen chloride, yet in practice no other acid works so well. Some, like phosphoric acid H_3PO_4, act too slowly, because they do not dissolve sodium chloride so readily. Others, like hydrofluoric acid HF, are too volatile, and the heat of the action would send them over with the hydrogen chloride in the form of vapor. Others, like nitric acid HNO_3, would react chemically with hydrogen chloride. Still others, like hydriodic acid HI, could be used only in aqueous solution, and the water would dissolve the hydrogen chloride produced, and prevent its

escape from the vessel. Aside from these objections, all the other acids are more expensive than sulphuric acid.

If various chlorides are used with the same acid, it will be found that the vigor of the actions is very different. In some, hydrogen chloride will be produced copiously without the assistance of heat. In others, there will be difficulty in showing that hydrogen chloride gas is produced at all. We must not hastily assume that this is owing to any greater chemical affinity in one case than another. More extensive experimentation will show that the *more soluble* chlorides as a rule give more vigorous effects than those which are less so (pp. 241, 280). Ammonium chloride with sulphuric acid would represent the former variety, while mercuric chloride with the same acid would represent the latter.

The egregious misconception that sulphuric acid is shown by this action to be "stronger" than hydrochloric acid was disposed of, so far as the science was concerned, half a century ago. But it survives in suburban chemical circles with remarkable tenacity. The fact, quaintly enough, is that the real relation in respect to activity (see p. 317) is just the reverse.

Physical Properties. — Hydrogen chloride is a colorless gas. It is sour in *taste*, and has a sharp *odor*. It is irritating, but not poisonous in small amounts.

Density ($H_2 = 1$), 18.23	Crit. temp., + 52°
Weight of 22.4 liters, 36.73 g.	Boiling-point (liq.), — 85°
Sol'ty in water (0°), 50,300 vols. in 100	Melting-point (solid), — 110°

The gas is one-fourth heavier than air. It is exceedingly *soluble* in water. The saturated solution at 15° contains nearly 43 per cent of the gas by weight. The concentrated hydrochloric acid of commerce contains from 35 to 39 per cent. On account of its great solubility and the small vapor tension of its solution (p. 212), the gas, on escaping into the air, condenses atmospheric moisture into a fog of drops of hydrochloric acid. Its extreme solubility may be shown by the "fountain experiment" (see ammonia, p. 511). On account of its high critical point, the gas may be liquefied by pressure alone. Both in the gaseous and liquefied states it is a non-conductor of electricity.

When the *concentrated* aqueous solution is heated, it is the gas and not the water which is driven out, for the most part. When the concentration has been reduced to 20.24 per cent the rest of the mixture distils unchanged at 108.6°. This occurs because, at this concentration, the gas enters into, and is carried off in, the

bubbles of steam in the same proportion in which it is present in the liquid. With a concentration above 20.24 per cent, more hydrogen chloride enters the bubbles, with one below 20.24 per cent, more water. Hence, if a dilute solution is used, *water* is the chief product of distillation (about 100°), but gradually the boiling-point rises and, when the concentration has reached 20.24 per cent once more, the same hydrochloric acid of **constant boiling-point** (108.6° at 760 mm.), as it is called, forms the residue (see Fig. 95).

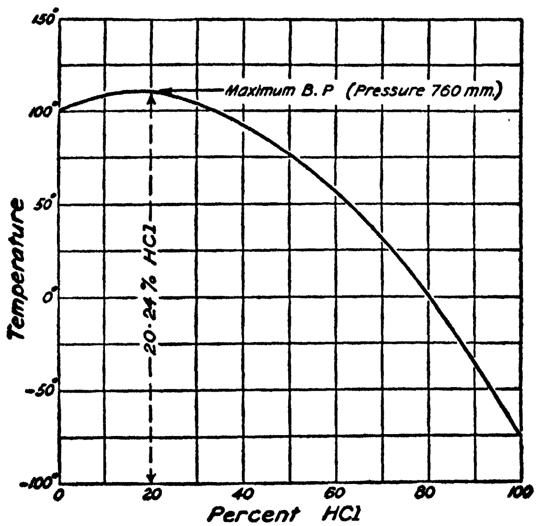


FIG. 95.—Composition of Saturated Vapor from Boiling Hydrochloric Acid Solutions (p = 760 mm.).

It is impossible to separate completely by distillation the components of mixtures which behave in this way. This must necessarily be the case whenever, as here, the vapor tensions of the components separately and those of all other mixtures are higher (and the b.-ps. lower) than that of one particular mixture. When, as is more often the case, one of the components has a vapor tension which is lower than that of the other and lower than that of any mixture of the two, this component will tend to remain behind, and separation can be effected. The separation of petroleum products (see p. 579) from one another illustrates the common case (see under Ethyl alcohol, p. 619, for the third possibility).

The composition of the mixture having the minimum vapor tension varies with the external pressure, and so does the boiling-point. At 300 mm. the constant boiling liquid contains 21.8 per cent of hydrogen chloride and boils at 84°; at 1520 mm. it contains 19.1 per cent of the gas.

The common belief that hydrochloric acid of constant boiling-point is a definite compound is without foundation. Compounds do not vary in composition with changes in pressure in this manner. Aqueous solutions of hydrogen

iodide, hydrogen bromide, and nitric acid behave in the same way. But solutions of oxygen, of ammonia, and of many liquids (*e.g.*, methyl alcohol) in water belong to the second of the two classes mentioned above, and the more volatile component often leaves the water entirely before much of the latter has evaporated.

Chemical Properties of Hydrogen Chloride. — Hydrogen chloride must be heated above 1800° before even 0.5 per cent of it is dissociated into hydrogen and chlorine (compare water, p. 173). Pure hydrogen chloride is therefore a *very stable* and, from a chemical point of view, rather an *inactive* substance. It has no action on *non-metals,* such as phosphorus, carbon, sulphur, etc. However, many of the more *active metals* (see p. 142), such as potassium, sodium, and magnesium, decompose it. Hydrogen is set free, and the chloride of the metal is formed:

$$2K + 2HCl \rightarrow 2KCl + H_2 \uparrow.$$

When hydrogen chloride is mixed with *ammonia* NH_3 the gases *unite* to form a cloud of fine, solid particles of ammonium chloride:

$$HCl + NH_3 \rightarrow NH_4Cl \downarrow.$$

It is worthy of note that this reaction does **not** take place if the two gases have both been exceedingly carefully dried. Hence it appears that here, as in many other cases (see pp. 233, 297), a trace of water functions as a necessary catalyst.

Chemical Properties of Hydrochloric Acid. — The solution of hydrogen chloride in water is an entirely different substance in its behavior from hydrogen chloride. (1) The solution is *sour in taste.* (2) *It changes the color of litmus,* a vegetable coloring matter, from blue to red. (3) It is a *conductor of electricity,* and is decomposed by the current, *hydrogen being liberated* at the negative wire (p. 134). (4) When the *metals preceding hydrogen* in the order of activity (p. 142) are introduced into hydrochloric acid, *hydrogen is displaced* and liberated.

In a later chapter (p. 293) we shall see that these four properties of hydrogen chloride in aqueous solution are properties common to *all substances called acids.* We may sum up the main properties of a solution of hydrogen chloride in water in one word, therefore, by saying that it is an **acid.**

Hydrochloric acid interacts with many other compounds in solution. In some instances, one of the new substances produced can be seen, because it appears as a precipitate. One such example has already been discussed in detail (see equation (2), p. 225). When hydrochloric acid is added to a solution of silver nitrate

(lunar caustic, $AgNO_3$), a precipitate of *silver chloride* ($AgCl$) is obtained, which is white and curdy in appearance. The other product, nitric acid (HNO_3), remains dissolved:

$$HCl + AgNO_3 \rightarrow AgCl \downarrow + HNO_3.$$

Other insoluble chlorides (see p. 248) can also be made conveniently by this plan. The formation of the precipitates, for example that of silver chloride, is used as a **test** for the presence of a soluble chloride in the solution.

Hydrochloric acid also **interacts** rapidly **with** most **oxides and hydroxides of metals,** as, for example, those of zinc:

$$ZnO + 2HCl \rightarrow ZnCl_2 + H_2O.$$
$$Zn(OH)_2 + 2HCl \rightarrow ZnCl_2 + 2H_2O.$$

Here no free hydrogen is obtained, since the oxygen in the oxide, and the hydroxyl in the hydroxide, unite with it to form water. In each case, however, the chloride of the metal is obtained. It may be noted, in passing, that all acids behave in a similar manner towards oxides and hydroxides of metals, giving water and a compound corresponding to the chloride. Dilute sulphuric acid, for example, gives sulphates.

Uses of Hydrochloric Acid. — This substance is used mainly as a source of chlorine. It is also directly employed for cleaning metals and in the manufacture of chlorides of metals. Some minor uses are shown in the accompanying diagram (Fig. 96). Although present in very small proportions (about 1 part in 500) in the gastric juice of the stomach, it is a most important component of this fluid. It is sometimes given as a medicine, when the natural supply is too small.

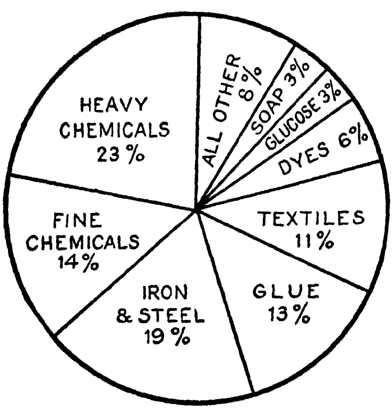


FIG. 96. Distribution of Hydrochloric Acid in Industry.

Double Decomposition. — In this chapter we have met again another variety of chemical change, already discussed briefly in an earlier chapter (p. 31). If we examine the equation for the action of silver nitrate on hydro-

chloric acid (p. 230), it will appear that the silver nitrate behaved as if it were decomposed into its two radicals, namely (Ag) and (NO_3). The hydrochloric acid similarly acted as if it were separated into its two radicals (H) and (Cl). The (Ag) then united with the (Cl) and the (H) was left with the (NO_3):

$$(Ag)(NO_3) + (H)(Cl) \rightarrow (Ag)(Cl) + (H)(NO_3).$$

Since both original substances acted as if they were decomposed, this whole change is called a **double decomposition.** It apparently consists of a simple exchange of radicals of the two substances concerned. Hence this type of reaction is often termed **metathesis** (Greek, *transposition*).

The hydrogen chloride was prepared by an action (p. 225) which, if we write it as follows, is seen to be of the same class:

$$(Na)(Cl) + (H)(HSO_4) \rightarrow (H)(Cl) + (Na)(HSO_4).$$

Other Ways of Obtaining Hydrogen Chloride. — Although never used for generating hydrogen chloride on a large scale, there is another important kind of action in which this substance is a product. When water acts upon the chlorides of non-metallic substances, like sulphur, phosphorus, and iodine, a double decomposition occurs. Since water is always one of the interacting substances, this kind of change, — **a double decomposition, involving water,** — is called **hydrolysis** (Greek, ὕδωρ, water, and λύσις, the act of loosing). Thus, when a little water is added to one of the chlorides of phosphorus, hydrogen chloride is formed. Besides this substance, the trichloride gives phosporous acid, and the pentachloride, phosphoric acid:

$$PCl_3 + 3HOH \rightarrow 3HCl + H_3PO_3.$$
$$PCl_5 + 4H_2O \rightarrow 5HCl + H_3PO_4.$$

Often, when a steady stream of hydrogen chloride is required, concentrated hydrochloric acid is placed in a generating flask, and concentrated sulphuric acid is allowed to trickle into it from a dropping funnel. The hydrogen chloride is less soluble in diluted sulphuric acid than in water (see p. 758) and escapes.

The Varieties of Chemical Change. — Almost all chemical changes belong to one or other of the varieties we have already met with and defined (pp. 15, 23, 130, 230). These, along with one example of each, are now placed together:

1. **Combination:** $Zn + S \rightarrow ZnS$.
2. **Decomposition:** $2KClO_3 \rightarrow 2KCl + 3O_2$.
3. **Displacement:** $Zn + H_2SO_4 \rightarrow H_2 + ZnSO_4$.
4. **Double Decomposition:** $AgNO_3 + HCl \rightarrow AgCl + HNO_3$.

In the first, *2 substances* give *1 substance*.
In the second, *1 substance* gives *2* (*or more*) *substances*.
In the third, *1 element* and *1 compound* give *1 element* and *1 compound*.
In the fourth, *2 compounds* give *2 compounds*.

This classification suffices for most purposes, although many complex reactions comprehend more than one variety, occurring either simultaneously or consecutively. But, for special kinds of cases, some other names are used. Thus, a **dissociation** (p. 173) is an action which belongs to *both* of the first two classes, because it is *reversible*. For example,

$$2H_2O \rightleftarrows 2H_2 + O_2.$$

The terms **oxidation** (p. 97) and **reduction** (p. 140) are connected with the particular substances, such as oxygen, which are concerned in the action. The foregoing classification pays no attention to the kinds of elements which are present. Thus, every decomposition is a decomposition. If it is reversible, then it is *also* a dissociation. If oxygen is set free, then it is a reduction *as well*.

Fifth Variety of Chemical Change: Internal Rearrangement. — It occasionally happens, especially in the case of compounds of carbon (see urea, p. 573), that one single kind of material turns into another single kind of material. Nothing is added and nothing removed, yet the new substance has different properties in every respect from the old. Most of those substances whose transformation is definitely assigned to this class contain several constituents, but a rough notion of this sort of chemical change may be obtained by considering the two forms of phosphorus. One of them is pale yellow in appearance, easily melted, and very easily ignited; the other is red, does not melt readily on being heated, and is difficult to ignite. The latter is made from the former by heating it continuously for some hours in a closed vessel at about 300°. As no material is taken up, the weight of the substance is unchanged, and yet, when the vessel is opened, the common phosphorus is found to have turned into the red variety. Now, we have seen that when substances have different properties they differ also in their constituent materials. Carrying out this idea, the hypothesis (or suggestion) has been made that, since here also the properties change, there must be some readjustment of the material, even in cases like this. Hence, we designate changes of this kind **internal rearrangements.** The composition of the material is unaltered, so we suppose its constitution to have become different. If the chemists ever decide to regard the change of water into ice or steam as a chemical phenomenon, all changes of state of aggregation would be placed in this fifth class. It is here only that the boundary between physics and chemistry (see. pp. 35–7) is at present difficult to define.

SODIUM HYDROXIDE

Preparation of Sodium Hydroxide NaOH from Salt. — The greater part of sodium hydroxide employed in chemical industries is manufactured by the electrolysis of sodium chloride in concentrated aqueous solution, the other product, chlorine, being of great commercial value also.

In the electrolysis of hydrochloric acid (p. 134), the hydrogen is set free at the negative pole (cathode). With a solution of sodium chloride we might expect to get free sodium at this pole. It will be recalled, however, that sodium is very much more active

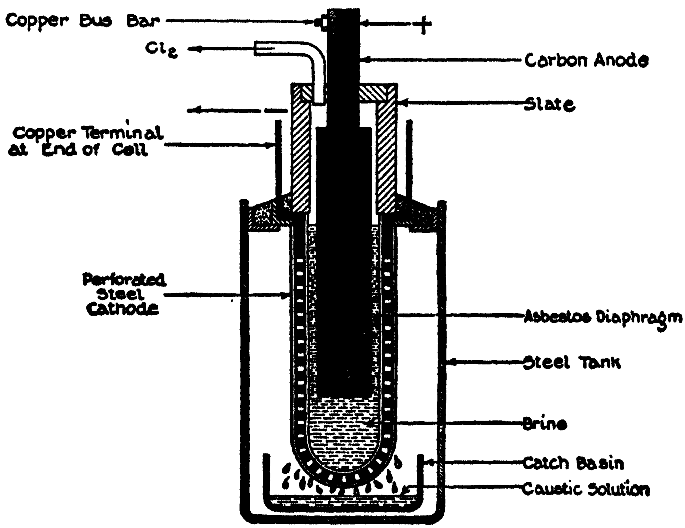


FIG. 97. Nelson Cell.

than is hydrogen, and indeed displaces hydrogen from water. Hence the electrical energy *sets free the more easily liberated element* — the hydrogen — and the sodium remains in the solution as sodium hydroxide (NaOH). The process is best shown by a diagram:

$$\begin{array}{rl} & \boxed{2Na}\,Cl \rightarrow Cl_2 \uparrow \text{ (positive pole)} \\ \text{(negative pole) } \uparrow H_2 \leftarrow 2H & \boxed{OH} \end{array}$$

The chlorine Cl_2 and hydrogen H_2, being liberated, leave behind in the solutions the constituents of 2NaOH:

$$2NaCl + 2H_2O + \text{Electrical energy} \rightarrow H_2 + Cl_2 + 2NaOH.$$

Cells like the Nelson cell (Fig. 97) are now most extensively used in commercial practice. A porous diaphragm of asbestos separates the perforated steel cathode from the carbon anode, which is immersed in a current of brine flowing through the cell between the electrodes. Chlorine is liberated at the anode and rises in bubbles to the surface of the solution. It is drawn off, dried, and compressed to liquid form in iron cylinders, or is made directly into bleaching compounds (p. 374). Sodium, as we have seen above, remains in the solution as sodium hydroxide, which collects around the cathode and flows out into a catch basin. It is purified from residual sodium chloride by fractional crystallization. Hydrogen is also liberated at the cathode, and is a valuable by-product of the process.

Physical Properties. — Sodium hydroxide is a *white* crystalline solid. It is exceedingly *soluble* in water. Its solution gives to objects the smooth, *soapy feeling* which is characteristic of alkalies. The solution is sometimes called **soda-lye,** and the solid (commercially always hydrated, about 24 per cent water) **caustic soda.**

Chemical Properties. — Sodium hydroxide is exceedingly *stable,* being melted, but not decomposed, by heating.

The *aqueous solution* possesses the following important properties. (1) The solution has a *bitter taste,* like soap or borax. (2) It *changes the color of litmus,* reddened by a trace of an acid, back again from red to blue. (3) It is a *conductor of electricity,* and is decomposed by the current, *oxygen being liberated* at the positive wire.

In a following chapter we shall see that these three properties of sodium hydroxide in aqueous solution are properties common to *all substances called alkalies.* The reader should at this point refer back to p. 229 and contrast these properties with those exhibited by *acids.*

Sodium hydroxide in solution *enters into double decomposition* with many substances. For example, with a solution of cupric chloride, sodium hydroxide gives a precipitate of cupric hydroxide:

$$2NaOH + CuCl_2 \rightarrow Cu(OH)_2\downarrow + 2NaCl.$$

As this equation shows, sodium hydroxide behaves in such actions as if it is decomposed into its two radicals, namely (Na) and (OH) (compare p. 231). The reaction appears to consist, essentially, of a transfer of (OH) radicals from (Na) to (Cu), and of (Cl) radicals from (Cu) to (Na).

Sodium hydroxide, in aqueous solution, also interacts with acids, as, for example, hydrochloric acid (compare p. 230) or sulphuric acid:

$$NaOH + HCl \rightarrow NaCl + H_2O.$$
$$2NaOH + H_2SO_4 \rightarrow Na_2SO_4 + 2H_2O.$$

Alkalies and Bases. — It will be seen that the chemical properties of sodium hydroxide solution may be summed up by saying that it is an **alkali.**

Solutions of the alkalies also *act upon animal matter, e.g.,* wool (p. 638), especially when hot, converting it largely into soluble substances. Consequently they are called *caustic alkalies.* They likewise act slowly upon the components of glass. For this reason a precipitate is often visible in the caustic soda reagent bottle, and the inner surface of the glass is always etched.

A very delicate **test** for an alkali is given by *phenolphthalein,* a colorless organic substance. One drop of phenolphthalein solution added to an alkali in water solution produces an intense *red* (when dilute, *pink*) coloration. Addition of excess acid renders the solution colorless again.

The alkalies, however, are simply the more active members of a much larger class of substances called **bases.** Solutions of the less soluble bases, of which cupric hydroxide is an extreme example, do not show, distinctly, all the properties exhibited by alkalies. Thus, those which are least soluble have, naturally, no taste, do not visibly affect litmus, do not conduct the electric current very well in solution, and are not soapy to the touch or corrosive towards glass. But they all show the tendency to double decomposition, in which the group (OH) is transferred, as it was from NaOH to $Cu(OH)_2$ in the foregoing example.

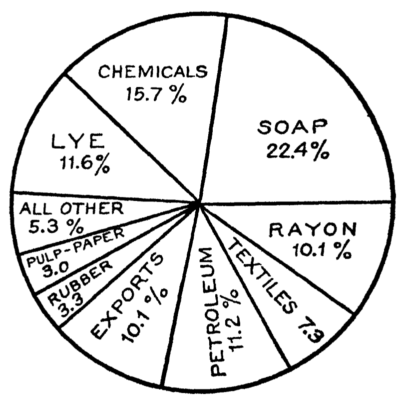


FIG. 98. Distribution of Caustic Soda in Industry.

Uses of Sodium Hydroxide. — Sodium hydroxide is used (see Fig. 98) in immense quantities along with fats, in the manufacture of soap. Some bleaching liquids are made by saturating it with chlorine. It is employed also in making many other sodium compounds which are used in the arts.

Exercises. — 1. Complete the equation $ZnCl_2 + H_2SO_4 \rightarrow ZnSO_4 +$, and attach the name of the substance to each formula in it.

2. Point out the differences in physical properties between oxygen and hydrogen chloride.

3. Give additional examples of the four varieties of chemical change (p. 232).

4. Classify (p. 232) the following actions: (*a*) the action of steam on iron (p. 130); (*b*) the rusting of iron; (*c*) the electrolysis of dilute hydrochloric acid (p. 134); (*d*) the effect of heating the hydrate of cupric sulphate (p. 175).

5. What weight of hydrogen is displaced by the action of 100 g. of zinc upon an excess of hydrochloric acid?

6. What weight of silver chloride is formed by the interaction of 5 g. of silver nitrate with excess of hydrochloric acid?

7. What weight of cupric hydroxide is formed by the interaction of 10 g. of blue-stone ($CuSO_4,5H_2O$) with excess of sodium hydroxide in aqueous solution?

8. What different modes of preparing chlorides have been mentioned in this chapter? Write the equation in each case.

9. Why does heating make the evolution of hydrogen chloride from a mixture of salt and concentrated sulphuric acid more rapid? Try to give three distinct reasons.

10. What is the weight-normality (p. 202) of a commercial sample of hydrochloric acid, containing 36 per cent HCl? If the density of the solution is 1.184, what is its volume-normality?

11. What weight of constant boiling-point hydrochloric acid (p. 228) would be required to react completely with 10 g. of zinc oxide (p. 230)?

12. For every kilogram of sodium hydroxide produced in the Nelson cell, what weights of chlorine and of hydrogen are also obtained?

13. Commercial caustic soda, 76 per cent NaOH (the rest is water), sells at $2.90 per 100 lbs. Liquid chlorine, in cylinders, sells at $2.00 per 100 lbs. Electrolytic hydrogen, compressed in cylinders to 150 atmospheres, sells at $10.00 per 100 lbs. What is the total value of the products obtained by the electrolysis of 1000 lbs. of sodium chloride in water solution?

14. What weight of sodium hydroxide, 76 per cent, will be required to react completely with 100 c.c. of a normal solution of hydrochloric acid? If this weight is dissolved in water, to what volume must the solution be made up so that its concentration is also normal?

15. Tabulate the uses of hydrochloric acid and of sodium hydroxide, and correlate each with some physical or chemical property of the substance.

16. It used to be stated that hydrochloric acid of constant boiling-point (see Fig. 95) was a definite compound $HCl,8H_2O$. Devise two distinct methods of demonstrating that this view is not valid.

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CHAPTER XIV

CHLORINE

Chlorine was first recognized as a distinct substance by Scheele (1774). He obtained it from salt by means of manganese dioxide, using the method described below (p. 240). It was supposed to be a compound containing oxygen until Davy (1809–1818) demonstrated that it was an element.

Chlorine does not occur free in nature. There are, however, many compounds of it to be found in the mineral kingdom. Sea-water contains a number of chlorides in solution. Of the 3.6 per cent of solid matter in sea-water, nearly 2.8 per cent is sodium chloride NaCl. During past geological ages the evaporation of sea-water has led to the formation of immense deposits of the compounds usually found in such water. Thus, at Stassfurt, such strata attain a thickness of over a thousand feet. Certain layers of these strata are composed mainly of sodium chloride (rock-salt). In other layers potassium chloride (sylvite), an indispensable fertilizer, and other compounds of chlorine occur.

Preparation. — Chlorine cannot be obtained with the same ease as oxygen. There are only a few chlorides, such as those of gold and platinum, which lose chlorine when heated, and they are too expensive or difficult to make for laboratory use. We employ therefore methods like those used for the preparation of hydrogen (compare p. 129). We may (1) decompose any chloride by means of electricity, just as, to get hydrogen, we electrolyzed a dilute acid (p. 134). Or (2) we may take some inexpensive compound of chlorine, such as hydrogen chloride (HCl), and by means of some simple substance which is capable of uniting with the other constituent — here oxygen serves the purpose — secure the liberation of the element. Or (3) — and this turns out to be the most convenient laboratory method — we may use a more complex action.

Electrolysis of Chlorides. — Hydrogen chloride and those chlorides of metals which are soluble in water are all decomposed when

a current of electricity is passed through the aqueous solution, yielding chlorine at the positive electrode (see pp. 134, 233). Since the chlorine is soluble in water, the effervescence due to its release is not noticeable until the liquid round the electrode has become saturated with the gas: Cl_2 (dissolved) $\rightleftarrows Cl_2$ (gas).

In commerce chlorine is now obtained chiefly by this method, sodium chloride or potassium chloride being the source of the element. The apparatus employed and the practical details of the process have already been described in connection with the manufacture of sodium hydroxide (p. 234).

Preparation of Chlorine from Oxygen and Hydrogen Chloride. — When hydrogen chloride and oxygen gases are heated, they interact very slowly to give water and chlorine. The action is greatly hastened by contact with copper chloride. Lumps of pumice, saturated with a solution of this catalyst (see p. 103), are placed in a tube. When the mixture of gases is passed over the heated pumice (Fig. 99), steam, chlorine, and about 20 per cent of unchanged oxygen and hydrogen chloride issue at the other end:

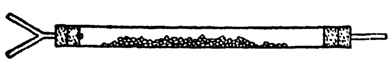


FIG. 99. Apparatus to Illustrate Deacon's Process.

Skeleton equation: $HCl + O_2 \rightleftarrows H_2O + Cl_2$.
Balanced equation: $4HCl + O_2 \rightleftarrows 2H_2O + 2Cl_2$.

Longer heating does not alter the proportion of the materials successfully transformed. Large quantities of chlorine were formerly manufactured by this method **(Deacon's process).**

That 80 per cent is changed, and 20 per cent unchanged, is due to the fact that the action is *reversible*. If we lead pure chlorine and steam through the tube (read the equation backwards), 20 per cent of hydrogen chloride and oxygen are formed. No more than 20 per cent is formed, because these products are continually being used up again and reproduce steam and chlorine. If one product could be separated (p. 177) from the other, to prevent the backward action, the yield could be raised to 100 per cent. But all the four substances are gases (in the hot tube) and mix perfectly.

The results here noted are interesting, because they show that, under the conditions of the experiment, oxygen is somewhat more active than chlorine in combining with hydrogen. The precise proportions of the four gases present at equilibrium depend on the temperature at which the reaction is carried out. In the commercial application of Deacon's process, this was near 345°.

Preparation of Chlorine from Hydrochloric Acid and an Oxidizing Agent. — The best way to make a supply of chlorine *in the laboratory* is to place potassium permanganate crystals ($KMnO_4$) in a flask (Fig. 100), and allow concentrated hydrochloric acid, previously mixed with an equal volume of water, to fall upon them drop by drop. The gas is rather soluble in water, and is best collected by displacing the air from bottles. When one bottle is full, it is stoppered and a fresh one substituted. To avoid the escape of the very irritating gas into the room the tube from the collecting bottle dips beneath sodium hydroxide solution, by which the gas is readily absorbed.

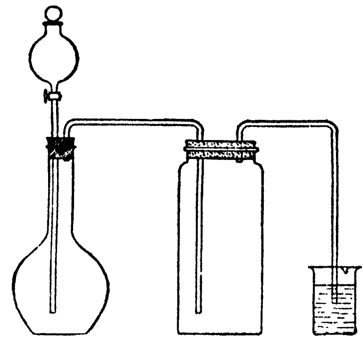


FIG. 100 Laboratory Preparation of Chlorine.

The essential feature of this reaction is that the oxygen of the potassium permanganate unites with the hydrogen of the hydrochloric acid to give water. The potassium and manganese take as much chlorine as they require to form their chlorides, KCl and $MnCl_2$. The rest of the chlorine is liberated:

Skeleton: $$KMnO_4 + HCl \rightarrow H_2O + KCl + MnCl_2 + Cl_2.$$

To convert all the oxygen of the $KMnO_4$ to water, we require 8HCl. The formation of KCl and $MnCl_2$ uses up 3 of the 8 atoms of chlorine thereby made available, leaving 5Cl to be liberated. Since this chlorine is obtained as Cl_2, it is necessary to *double* our quantities throughout:

Balanced: $$2KMnO_4 + 16HCl \rightarrow 8H_2O + 2KCl + 2MnCl_2 + 5Cl_2.$$

This action is an *oxidation of the hydrogen chloride* by the permanganate. The potassium permanganate, which supplied the oxygen, is called the *oxidizing agent*. Since the permanganate *lost* oxygen, it was itself *reduced*. In all oxidations one substance is oxidized and another reduced.

Deacon's process (p. 238) is also an oxidation of hydrogen chloride (by free oxygen). The oxygen is reduced to water. It is true that no oxygen is actually introduced into the hydrogen chloride as a whole. The removal of hydrogen from combination with the chlorine is, however, the first step towards the introduction of oxygen into combination with hydrogen, and is essentially an oxidation (see p. 376).

Other Means of Oxidizing Hydrogen Chloride. — Many other compounds of oxygen with metals interact with hydrochloric acid to give free chlorine. Lead dioxide PbO_2, potassium dichromate $K_2Cr_2O_7$, and manganese dioxide MnO_2, are of this nature. The last, being inexpensive, is commonly used in making chlorine. Being an almost insoluble substance, however, the manganese dioxide acts much more slowly than does the potassium permanganate, which is readily soluble. A large amount of the materials, and the aid of heat, are required to secure a rapid stream of chlorine.

Manganese Dioxide and Hydrogen Chloride. — The action of manganese dioxide upon hydrochloric acid is an instructive one. It is a **general rule,** of which we shall meet many applications, that **when an acid interacts with an oxide of a metal,** there are two constant features in the result, namely: (1) **The oxygen of the oxide combines with the hydrogen of the acid to form water,** and (2) **the metal of the oxide combines with the acid radical of the acid** (compare p. 230). Here the skeleton equation should be $MnO_2 + HCl \rightarrow H_2O + MnCl_4$. With O_2, to form water, 4HCl is required, and the product is $2H_2O$. Hence the equation is:

Balanced: $$MnO_2 + 4HCl \rightarrow 2H_2O + MnCl_4.$$

This is, undoubtedly, what happens in the first place. The products actually obtained on heating the mixture, however, are water, manganous chloride $MnCl_2$ and chlorine. We owe the chlorine to the fact that the tetrachloride is unstable. At low temperatures it decomposes into manganese trichloride ($MnCl_3$) and chlorine. When the mixture is warmed, the $MnCl_3$ breaks down further into $MnCl_2$ and chlorine. The complete series of reactions may be represented in one equation as follows:

$$MnO_2 + 4HCl \rightarrow 2H_2O + MnCl_2 + Cl_2. \qquad (1)$$

The action (1) is of a type very common in chemistry. It is more complex even than double decomposition (p. 231), and, unlike this, its results cannot be anticipated by guessing. If we had used *manganous oxide* MnO, we should have had a double decomposition:

$$MnO + 2HCl \rightarrow H_2O + MnCl_2, \qquad (2)$$

but we should obtain no chlorine. Perhaps the simplest way to describe the difference between these two actions is in terms of the valence of the man-

ganese. In $Mn^{IV}O_2^{II}$ the element is quadrivalent. This means that its atomic weight professes to be able to hold four atomic weights of a univalent element. The four valences of oxygen ($2O^{II}$) can do the same thing. In equation (1) the oxygen fulfils this promise by taking $4H^I$. But the Mn^{IV} can hold only $2Cl^I$, permanently, and lets the other $2Cl^I$ go free. In other words, the *valence* of the atomic weight of *manganese changes* in the course of the action. In equation (2), on the other hand, the manganese is bivalent to start with ($Mn^{II}O^{II}$), and is able to retain the amount of chlorine ($2Cl^I$) equivalent to O^{II}. Actions like that of manganese dioxide in (1) are classed as oxidations. The hydrogen chloride, or rather half of it, is oxidized. A graphic mode of writing may make this remark clearer:

$$Mn^{IV}\begin{cases} {=}O + 2HCl \rightarrow H_2O + Mn^{II}Cl_2 \\ {=}O + 2HCl \rightarrow H_2O + Cl_2 \end{cases}$$

The upper half is a double decomposition, the lower an oxidation by half the combined oxygen of the dioxide. The same explanation applies to the interaction of lead dioxide with hydrochloric acid.

In practice, instead of employing aqueous hydrochloric acid we frequently use the materials from which it is prepared, namely, common salt and concentrated sulphuric acid (p. 224), along with the manganese dioxide. Under those circumstances, the action appears more complex, but is simply a combination of the two chemical changes, and is represented by the equation:

$$MnO_2 + 2NaCl + 3H_2SO_4 \rightarrow 2H_2O + 2NaHSO_4 + MnSO_4 + Cl_2.$$

Kinetic-Molecular View of these Actions.—In preparing chlorine with manganese dioxide, the gas is produced rather slowly. The situation is that we have placed together manganese dioxide in a granular form and water which contains hydrogen chloride in solution. The dioxide is very insoluble in water, and consequently the effective amount present, since it must dissolve before it can meet the acid, is exceedingly small: MnO_2 (solid) $\rightleftarrows$ MnO_2 (dslvd.). The finer the pulverization, and the larger the amount of the oxide, the less will be the delay from this cause. On the other hand, the acid contains originally only about one molecule of hydrogen chloride for every five of water and, as the former is used up, the scarcity of the active substance becomes greater.

Again, we heat the mixture on a water bath so as to hasten the process (p. 99) by raising the temperature to about 90°. When we prepared oxygen, we forced the temperature up with a naked Bunsen flame until, at about 300°, a sufficiently rapid stream of the gas was secured. The iron and sulphur (p. 22) we raised nearly to a red heat. Here the conditions make stronger heating impossible. No aqueous solution of hydrogen chloride can be raised above 108.6°, the maximum boiling-point (p. 228). But we must not carry the heating so far as 108.6°, because even below this point the concentrated acid

gives off gaseous hydrogen chloride freely. If we did, we should contaminate our chlorine and at the same time lose a part of one of the ingredients on which the action depends. Intelligent chemical work always demands a careful consideration of purely physical facts of this description.

On the other hand, **when potassium permanganate is employed** (p. 239), the chlorine is evolved very rapidly. The permanganate is fairly soluble in the cold (6.5 parts in 100 of water at 15°), and becomes rapidly more soluble as the heat of the reaction raises the temperature of the liquid. Then, too, the permanganate is a more active oxidizing agent, at equal concentrations, than is manganese dioxide, and so attacks the hydrochloric acid more rapidly.

Physical Properties. — Chlorine differs from the gases we have encountered so far in having a strong greenish-yellow tint (Greek, χλωρός, pale green), a fact which gave rise to its name. It possesses an exceedingly disagreeable odor and exercises a powerful, irritating effect upon the membranes of the nose and throat. Alcohol vapor or ammonia, when breathed, relieves the irritation.

Density ($H_2 = 1$), 35.79	Boiling-point (liq.), — 34.6°
Weight of 22.4 l., 72.13 g.	Melting-point (solid), — 102°
Sol'ty in water (20°), 215 vols. in 100	Vap. tension (liq.) 0°, 3.66 atmos.
Crit. temp., + 144°	Vap. tension (liq.) 20°, 6.62 atmos.

Since a liter of air weighs 1.293 g., chlorine (wt. 1 liter, 3.22 g) is two and a half times as heavy. In solubility in water it stands between slightly soluble gases, like oxygen and hydrogen, and those which are extremely soluble. The solution is called **chlorine-water,** and is of a rather complex nature (see p. 245).

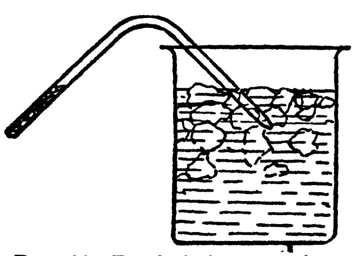


FIG. 101. Faraday's Apparatus for Liquefaction of Chlorine.

When chlorine-water is cooled with ice, a compound, **chlorine hydrate** $Cl_2,8H_2O$, crystallizes out. Faraday (1823) placed this substance in the closed limb of a bent glass tube, sealed the open end, and placed the empty limb in cold water (Fig. 101). When the hydrate was gently warmed, chlorine gas was given off and was liquefied by its own pressure in the cold part of the tube.

Chlorine was first liquefied by Northmore (1806). The critical temperature (p. 124) is exceptionally high (144°), so that at all ordinary temperatures the gas can be liquefied by compression alone. It forms a yellow liquid which, contained in steel cylinders,

is now an article of commerce. On being cooled below —102°, it gives a pale-yellow solid.

Chemical Properties. Reactions with Other Elements.— Chlorine is an element with about the same degree of activity as oxygen (compare p. 238), and it unites with very much the same list of other elements.

All the familiar **metals,** with the exceptions of gold and platinum, combine readily with chlorine. Copper leaf (Dutch metal, used in "gilding"), or heated copper foil, *burns* in the gas, giving a fog of solid cupric chloride $CuCl_2$. When powdered antimony (cold) or iron powder (warmed) is thrown into a jar of chlorine, red hot particles of their chlorides, $SbCl_3$ or $FeCl_3$, fall to the bottom:

Skeleton: $Sb + Cl_2 \rightarrow SbCl_3.$
Balanced: $2Sb + 3Cl_2 \rightarrow 2SbCl_3.$

Sodium burns brilliantly in chlorine, giving sodium chloride. That a shining metal and a poisonous irritant like chlorine, in uniting, should yield a mild, household article like common salt illustrates very well the extraordinary nature of chemical change.

When thoroughly freed from moisture, chlorine no longer combines with metals like copper and iron. *Water* seems to be needed as a *catalyst,* in these, as well as in hundreds of other chemical actions.

Phosphorus burns in chlorine with a rather feeble light, producing primarily phosphorus trichloride PCl_3, a liquid (b.-p. 74°). If excess of chlorine is present, then, as the trichloride cools, it combines to form the solid pentachloride PCl_5 (see p. 193). **Sulphur,** when heated, unites more slowly, giving sulphur monochloride S_2Cl_2, a liquid used in vulcanizing rubber.

A jet of burning **hydrogen,** lowered into a bottle of chlorine, continues to burn, giving hydrogen chloride HCl, the presence of which is shown by the fog produced by allowing the gas to come in contact with moist air:

$$H_2 + Cl_2 \rightarrow 2HCl.$$

Hydrogen and chlorine, mixed, do not combine when cold, provided strong light is excluded. But sunlight, or light from burning magnesium ("flashlight powder"), starts the combination, which

occurs with explosive violence. Plunging a lighted taper into the mixture has, of course, the same effect.

The function of the light here is entirely different from that in the decomposition of silver chloride (p. 32). In the latter case light was used to maintain the change, which comes to a stop whenever the light is withdrawn: the action was not self-sustaining and consumed energy. The union of hydrogen and chlorine is self-supporting, and a minimum of light only is needed to start it (compare p. 101). The action of the light is catalytic.

Chemical Properties. Reactions with Compounds. — Because of its activity toward hydrogen, chlorine removes hydrogen from many compounds. Thus, if a lighted wax taper be plunged into chlorine, it continues to burn, though with a feebler flame. Dense smoke, composed of particles of free carbon, rises from the flame. Blowing the breath into the jar, afterwards, gives the fog due to hydrogen chloride. Thus the presence of hydrogen and carbon in the wax of the taper is proved. From this we learn, also, that chlorine has a relatively small tendency to combine with carbon. A few drops of warm *turpentine* ($C_{10}H_{16}$) upon a slip of filter paper will blaze up in chlorine, giving hydrogen chloride and an immense cloud of soot (finely-divided carbon):

Skeleton: $C_{10}H_{16} + Cl_2 \rightarrow C + HCl.$
Balanced: $C_{10}H_{16} + 8Cl_2 \rightarrow 10C + 16HCl.$

The action on turpentine is a **substitution** of the carbon by the chlorine. Of a somewhat similar nature (see, however, p. 245) is the **displacement** by chlorine of the bromine or iodine in bromides or iodides, dry or in solution. Thus with potassium iodide KI we have the reaction:

$$2KI + Cl_2 \rightarrow 2KCl + I_2.$$

The iodine, when moist, is deep brown in color. A mere trace of chlorine, liberating a trace of iodine, gives no visible effect. But if some starch is present, even a trace of free iodine yields a deep blue color. This reaction is used as a test for chlorine, for free iodine from any source, and for starch (p. 7). To test for chlorine, strips of filter paper, dipped in starch emulsion (starch boiled with much water and cooled) to which a few drops of potassium iodide have been added, are used. *Combined* iodine, as in potassium iodide, has no effect upon starch. Combined chlorine, as in sodium chloride, has no action upon the prepared strips of paper — free chlorine is required.

Chlorine also unites directly with many compounds. Thus, one of the oxides of carbon, carbon monoxide CO, when mixed with chlorine and exposed to sunlight gives drops of a volatile liquid (b.-p. 8.2°) known as **phosgene** $COCl_2$.

Substitution resembles displacement (p. 130) in that an element and a compound interact, and the element takes the place of one unit in the composition of the latter. In the above action, one unit of chlorine takes the place of one unit of hydrogen. But *the latter is not liberated;* it combines with another unit of chlorine. The action resembles double decomposition, excepting that one of the substances is not a compound, but a diatomic element. The name used is intended to fix the attention on the *compound* and on the fact that one unit has been *substituted* for another in it. This conception is a favorite one in the chemistry of compounds of carbon (see p. 584).

Chlorine-Water. — We have seen that chlorine seizes the hydrogen in turpentine. We have also learned that it combines with the hydrogen in steam, reversing Deacon's process to the extent of 20 per cent. It also acts upon **cold water,** when dissolved in the latter, although in a similarly incomplete way. The substances formed are hydrochloric acid and **hypochlorous acid** $HOCl$:

$$H_2O + Cl_2 \rightleftarrows HCl + HOCl.$$

With half-saturated chlorine-water at 10° — that is, water containing about an equal volume of chlorine gas (see p. 242) — about one-third of the chlorine is changed into the acids. Thus, chlorine-water (the solution) is a mixture containing dissolved chlorine and two acids. Hypochlorous acid (see p. 370) is of especial interest because it is a very active substance, much used as an oxidizing agent and for bleaching.

The so-called bleaching action of "chlorine" is almost always the result of oxidation of the coloring matter by hypochlorous acid (see p. 372). Chlorine and the dye in the cloth, even when only moderately dry, show no tendency to interaction. This may be demonstrated by collecting some chlorine in a stoppered bottle in the bottom of which a little concentrated sulphuric acid stands. A piece of colored calico may be attached by a pin to a cork stuck in the bottom of the stopper and so suspended in the gas (Fig. 118, p. 372). After twenty-four hours no action will be found to have occurred. Yet if the rag is first moistened, the bleaching is almost instantaneous. Hence this bleaching action is treated under the properties of hypochlorous acid.

The action between chlorine and water comes to a standstill when one-third completed, because the two acids which are formed

re-interact to reproduce chlorine and water (read the equation backwards). The action is thus *reversible*. When the solution is exposed to sunlight, the hypochlorous acid decomposes and oxygen gas is liberated and escapes:

$$2HOCl \rightarrow 2HCl + O_2 \uparrow .$$

Since this removes the hypochlorous acid, on whose interaction with the hydrogen chloride the reverse action depends, the forward action *proceeds under continuous illumination* gradually *to completion*. Hence an aqueous solution of chlorine must be kept in the dark, since otherwise, after a time, a dilute solution of hydrogen chloride alone remains.

The reader should note here the displacement of the equilibrium, a chemical one in this case, in consequence of the annulment of one of the opposing tendencies (p. 170). Through the destruction of the hypochlorous acid, one of the tendencies, namely, that represented in the backward action, becomes inoperative. The forward action is not itself assisted, but it is no longer impeded, and so proceeds to completion.

So-called "Nascent Oxygen." — The oxidizing action of chlorine water was formerly attributed to "nascent oxygen" — oxygen in the state of being born. It was supposed that the chlorine preëmpted the hydrogen of the water, without actually combining with it, and so left the oxygen in a distracted condition in which it was more active than free oxygen! But all this speculation occurred before we knew that there was hypochlorous acid in chlorine-water. A pure solution of this acid performs all the oxidations that chlorine-water can bring about. So that, since we now have to choose between a substance we know to be present, and to be perfectly capable of doing the work, and an imaginary, ill-defined entity, the scientific method naturally demands that we attribute the effect to the substance. In this connection, the correct name for "nascent oxygen" is, therefore, hypochlorous acid.

It is, in any case, time that the term, and the idea, of "nascent oxygen" should be eliminated from the science. This material is imaginary — it has never been isolated or studied quantitatively. If it is an allotropic form of oxygen, it must have properties and a degree of activity that can be defined quantitatively. But this cannot be done, because it has not always the same activity. Thus, if all oxidizing agents perform their oxidizing by means of "nascent oxygen," it is curious that ozone oxidizes indigo (p. 365) instantly and easily, while hydrogen peroxide does not, also that chloric acid $HClO_3$ oxidizes hydrochloric acid rapidly, while perchloric acid $HClO_4$ does not. (For explanation of oxidation by oxidizing agents, see pp. 365, 373.) If we mean that, when the free elements are not present and yet compounds containing them interact, we must assume that the elements are in the nascent condition, then we should be consistent, and explain the action of sulphuric acid on

sodium chloride as being due to nascent chlorine and nascent hydrogen! All double decompositions would demand the same mode of explanation! Finally, since every oxidation is accompanied by a reduction, when we assume the presence of nascent oxygen, to be consistent, we ought to assume the presence of nascent hydrogen also: each such case involves a twin birth. The conception will not bear careful examination.

Uses of Chlorine. — Large quantities of chlorine are manufactured for the preparation of bleaching materials (*e.g.*, in the pulp and paper industry) and disinfecting agents (see Fig. 102). In disinfection, the minute germs of disease and putrefaction are acted upon either by the chlorine or by the hypochlorous acid formed by its interaction with water, and instantly their life is destroyed.

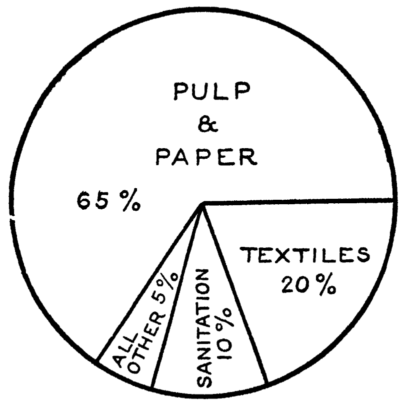


Fig. 102. Distribution of Liquid Chlorine in Industry.

Chlorine is also a substance of great technical importance in connection with the manufacture of certain explosives and dyestuffs. For the use of chlorine and of compounds containing chlorine in gas warfare, see Chapter XXXVIII.

Chemical Relations of the Element.* — In the chlorides, an atomic weight of chlorine is equivalent to one atomic weight of hydrogen or of sodium. The element is, therefore, **univalent** (p. 146). It never shows any higher valence than this, save in its oxygen compounds (see Chapter XXII). The oxides of chlorine interact with water to give acids, and the element is, therefore, to be classed as a **non-metal** (p. 174). It belongs to that **group** of the non-metals called the **halogens,** as a consideration of some others of its relations will show (see Chapter XX).

* In accordance with the distinction that must be drawn (p. 26) between the element as a variety of matter *in combination*, and the elementary substance or free form of the element, and to avoid a common source of confusion, we shall always give only the behavior of the elementary *substance* under the title *chemical properties*. The characteristics which distinguish the *compounds* of the element as a class from, or relate them as a class to, the compounds of other elements will then appear in a separate section under the title "Chemical Relations."

The chlorides are described individually under the other element which each contains. The majority of the chlorides of the metals are easily soluble in water. The chief exceptions are silver chloride AgCl, mercurous chloride (calomel) HgCl, cuprous chloride CuCl, and lead chloride $PbCl_2$. The last of these is on the border line as regards solubility. An appreciable amount dissolves in cold water, and a considerable amount in boiling water (see Table of Solubilities, inside the cover at the front of this book). Various modes of preparing chlorides have been indicated in this and in the previous chapter.

Confirmation of the Formulæ Cl_2 and H_2. — According to Avogadro's law, there are equal numbers of molecules in equal volumes of these gases. When hydrogen and chlorine combine, one volume of each of these gases gives two volumes of hydrogen chloride. Let us imagine the experiment to be made with minute volumes holding one thousand molecules each:

Hydrogen		Chlorine		Hydrogen Chloride	
1000 mols.	+	1000 mols.	→	1000 mols.	1000 mols.

It appears from this that 2000 molecules of hydrogen chloride come from 1000 molecules of hydrogen and 1000 molecules of chlorine. Now, each molecule of hydrogen chloride contains at least one atom of hydrogen, so that the 1000 molecules of hydrogen must have given at least 2000 atoms of hydrogen, one for each molecule of the compound. Hence *each molecule of hydrogen contains at least two atoms.* The same is true of each molecule of chlorine. We have no reason, however, for supposing that there are more than two atoms in either molecule; no substance is known which contains *less than* 1.008 g. hydrogen or 35.46 g. chlorine in its unit weight (p. 187). Hence the conclusion is confirmed which we reached before (p. 189), namely, that the formulæ of the free gases are H_2 and Cl_2, and that single atoms of the elements occur only in combination (as in NaCl, HCl, etc.). The molecular equation for their interaction *must* be written:

$$H_2 + Cl_2 \rightarrow 2HCl.$$

Calculations

Familiarity with the interpretation of **molecular equations** is best obtained by making simple calculations based upon their common uses in chemistry.

Weights. — When a problem in regard to weights of material used or produced in a given action is to be solved, the molecular equation is to be written and the weights inserted beneath the formulæ. The mode of calculation has been described already (pp. 82-3).

Weights and Volumes. — When a problem involving **weights and volumes** is to be solved, the molecular equation is to be written, and both the weights and volumes are to be inserted. Note, however, that only the volumes of the substances *in the gaseous condition* are considered.

For example, what volume of oxygen is obtained from 60 g. of potassium chlorate? The molecular equation, made as already described (p. 81), together with the full interpretation, is as follows:

$$\begin{array}{llll} & 2KClO_3 & \rightarrow \quad 2KCl & + \quad 3O_2. \\ \textit{Weights:} & 2(39.1 + 35.46 + 48) & 2(39.1 + 35.46) & 3 \times 32 \\ & 245.1 \text{ g.} & 149.1 \text{ g.} & 96 \text{ g.} \\ \textit{Volumes:} & & & 3 \times 22.4 \text{ l.} \end{array}$$

Observe that no volumes are given under the chlorate and chloride of potassium. This is because their volumes in the *gaseous* condition can be of no practical use, since they are solids which may be melted, *but not vaporized* during this, or any action in which we employ them. Now, as to the problem in hand, it is concerned with a weight of potassium chlorate and a volume of oxygen. Reading from the equation, our information on *these* points is that 245.1 g. of potassium chlorate give 67.2 liters of oxygen at 0° and 760 mm., and the question is: What volume will 60 g. give? By proportion 245.1 g. : 60 g. :: 67.2 liters : x liters, whence $x = 16.45$ liters. If a different temperature and pressure had been specified, either the volume in the equation or the answer would have had to be converted, by rule, to the given condition.

It saves time not to write out, as above, the whole interpretation, but only the parts required. For example, if the question is: What volume of chlorine is needed to give 25 g. of aluminium chloride? we may, if we choose, omit all the data excepting the volume of the chlorine and the weight of the aluminium chloride, thus:

$$\begin{array}{lll} 2Al \quad + & 3Cl_2 & \rightarrow \quad 2AlCl_3 \\ & 3 \times 22.4 \text{ liters} & 2 \times 133.5 \text{ g.} \end{array}$$

The volume of chlorine required is $25 \times 3 \times 22.4 \div (2 \times 133.5)$ liters.

Relative Volumes Alone. — If the question concerns **relative volumes** only, then it is simplest to use the interpretation of the equation in terms of molecules. For example: What relative volumes of hydrogen chloride and oxygen interact in Deacon's process (see p. 238)? The molecular equation is:

$$4HCl + O_2 \rightarrow 2H_2O + 2Cl_2.$$

Molecules: 4 1 2 2

Since equal numbers of molecules of gases occupy equal volumes, the proportion 4 molecules of hydrogen chloride to 1 molecule of oxygen shows the ratio to be 4 : 1 by volume. Similarly, every 4 molecules of hydrogen chloride actually taking part in the reaction give 2 molecules of chlorine, so that the volume of the Cl_2 produced is only one-half of that of the HCl which is used up.

In regard to the water, since that is not a gas at common temperatures, the question, if asked, must be more specific: What are the relative volumes of *steam* and chlorine in the product, as commonly delivered by his action? They are 2 : 2, or 1 : 1. What are the relative volumes of water and chlorine, after the products have cooled to room temperature? The water is no longer a gas, so that it occupies, relatively, almost no volume (p. 165).

Another Example. — When we know the molecular formulæ of the single substances concerned in an action, the equation can be made, and **the relative volumes determined, without actual measurement.** For instance: What volume-change will be observed when a mixture of equivalent amounts of carbon monoxide CO and oxygen has exploded, and the temperature has once more reached that of the room? The only product of the reaction is carbon dioxide CO_2. The equation representing the reaction, when properly balanced, *must* be written:

$$2CO + O_2 \rightarrow 2CO_2.$$

Three molecules, therefore, give two, throughout the whole mass, and therefore three volumes will become two, if the pressure and temperature are the same at the beginning and end of the action.

If we remember that all volatile compounds of carbon and hydrogen burn to form water and carbon dioxide, the molecular equation for any such combustion may easily be made, and the volumes of all the materials ascertained. When water is a product, only its volume as steam is given by the equation.

Relative Densities of Gases. — Knowing by heart the molecular formulæ of gaseous substances, as we must know them for many

purposes, it is unnecessary to burden our minds with other data in regard to **the relative weights of gases.** Is hydrogen chloride (HCl) heavier or lighter than carbon dioxide (CO_2)? These formulæ represent the weights of equal volumes (22.4 liters), namely, 36.468 g. and 44.00 g., respectively. Hence the former gas is a little lighter.

Remembering that the G.M.V. of air weighs 28.955 g. (p. 185), we can compare the weight of any gas with that of air in the same way. What are the relative weights of acetylene (C_2H_2, p. 191) and sulphur dioxide (SO_2) as compared with air? The G.M.V. cube holds formula-weights of the first two, namely 26.016 g. and 64.06 g., and 28.955 g. of air. Hence acetylene is a little lighter than air, and sulphur dioxide more than twice as heavy.

Exercises. — 1. What would be the results of electrolyzing aqueous solutions of: (*a*) potassium chloride; (*b*) cupric chloride (compare p. 233)?

2. How should you separate the chlorine and the steam produced by Deacon's process?

3. Make equations showing the interactions with hydrochloric acid of: (*a*) lead dioxide PbO_2; (*b*) potassium dichromate $K_2Cr_2O_7$. The metals form $PbCl_2$, KCl, and $CrCl_3$, respectively.

4. Make equations for the union of chlorine with: (*a*) copper; (*b*) sodium; (*c*) iron; (*d*) phosphorus; (*e*) sulphur.

5. When plunged into chlorine, a jet of illuminating gas continues to burn. A stream of soot rises from the flame, however, and blowing the breath into the jar, afterwards, produces a fog. What do you infer as to the constituents of illuminating gas?

6. What information is conveyed by the fact that the formula of the chloride of sulphur is written S_2Cl_2, and not SCl?

7. What facts led us, in Chapter XI, to the conclusion that the molecular weight of chlorine was 70.92 while its atomic weight was 35.46?

8. What are the relative densities of: (*a*) oxygen and chlorine; (*b*) hydrogen and hydrogen chloride; (*c*) hydrogen and air; (*d*) methane CH_4 and air?

9. What volume of hydrogen chloride at 0° and 760 mm. is obtained by the interaction of 65 g. of sodium chloride and an excess of sulphuric acid (p. 225)?

10. What weight of zinc is required to make 100 liters of hydrogen, at 10° and 750 mm., by displacement from hydrochloric acid (p. 133)?

11. What are the relative volumes of the initial substances and of the final products in the interactions between: (*a*) turpentine vapor and chlorine; (*b*) oxygen and carbon disulphide vapor (giving SO_2 and CO_2)?

12. What are the relative volumes of the products in the decomposition of: (*a*) mercuric oxide; (*b*) chlorine monoxide Cl_2O (chlorine and oxygen are formed)?

13. What are the relative volumes of the volatile substances concerned in the action of water vapor on iron (p. 141)?

14. What volume of oxygen at 10° and 750 mm. is obtainable by heating 50 g. of potassium chlorate?

15. What volume of oxygen at 20° and 760 mm. is required to convert 16 g. of iron into rust (Fe_2O_3)?

16. Write out the molecular equations for the interactions of acetylene and oxygen (p. 250), and of alcohol vapor (b.-p. 78°) and oxygen. Deduce the volume relations of the initial substances and of the products at 0° and at 100° in each case.

17. The molecular weight of butane is 58.08. What is its density referred to air, and what is the weight of 1 liter at 0° and 760 mm.? It contains 82.64 per cent carbon and 17.36 per cent hydrogen. What is the formula of the substance (pp. 79, 185)? Exploded with oxygen it forms carbon dioxide and steam. What will be the relative volumes of the materials before and after the interaction (p. 250)?

18. What are the relative weights of equal volumes of hydrogen sulphide (H_2S), and hydrogen iodide (HI), compared with air (p. 251)?

19. What volume of chlorine at 18° and 740 mm. will be obtained by the action of excess $KMnO_4$ on 100 g. of 20 per cent hydrochloric acid? *Do not calculate the weight first.*

20. What volume of chlorine at 15° and 770 mm. will be obtained by the action of excess MnO_2 on 100 c.c. of 6 *N* hydrochloric acid?

21. What weight of potassium dichromate $K_2Cr_2O_7$ should we require to add to excess concentrated hydrochloric acid to obtain 22.4 liters of chlorine at 0° and 760 mm.?

22. From an inspection of the equations, state what will be the relative volumes of chlorine obtainable by the action of excess $KMnO_4$, $K_2Cr_2O_7$ and MnO_2 respectively on equal quantities of concentrated hydrochloric acid.

23. Assuming a yield of 80 per cent, calculate what volume of chlorine at 5° and 780 mm. will be obtained by passing 100 g. of hydrogen chloride with an equivalent amount of oxygen through Deacon's process.

24. Devise a method of proving that the formula of chlorine hydrate is $Cl_2,8H_2O$.

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CHAPTER XV

ENERGY AND CHEMICAL CHANGE

In the description of both chemical and physical changes, the fact that heat was evolved or absorbed has frequently been mentioned. In several instances a current of electricity has been used to produce chemical change. It is now necessary to collect these scattered facts and classify them for future use.

Physical Accompaniments of Chemical Change. — When iron and sulphur combined (p. 22), and when iron burned in oxygen or copper in chlorine, much *heat was developed.* On the other hand, the decomposition of mercuric oxide, as was pointed out (p. 23), owed its continuance to the persistent application of heat and ceased as soon as the source of heat was withdrawn. Here, apparently, *heat was consumed* during the progress of the change, and the chemical action was limited by the amount of heat supplied. The **production or consumption of thermal energy** may, therefore, be a feature of chemical change.

In the burning of iron or magnesium in oxygen, and in the actions of chlorine on copper and turpentine, **light** was also produced. Conversely, silver chloride (p. 32) can be kept any length of time in the dark, but in sunlight it becomes first bluish and then brown, simultaneously giving off chlorine gas and finally leaving only silver as a fine powder. Silver bromide or iodide, in photographic plates, films, and paper, is changed by light in a similar way, liberating the bromine or iodine. It would appear, therefore, that **radiant energy may be given out or consumed** in connection with chemical change.

We have seen (p. 238) that a current of **electricity** may be employed to decompose hydrochloric acid and other chlorides, and the battery or other source of the current must be kept going or the chemical change stops. Similarly, if we dip two platinum wires connected with the opposite poles of a battery or dynamo into a solution of nitrate of silver $AgNO_3$, we observe the instant production of a coating of silver on the negative wire. By preparing the solution properly and allowing the **electricity** to flow through it

for a sufficient length of time, all of the compound can be decomposed and all its silver deposited. This release of the silver from chemical combination, and liberation of the metal at the electrode, goes on only so long as the current of electricity is employed, and electrical energy is consumed in the process. Very many substances can be decomposed in this way.

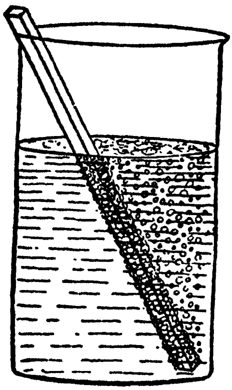


Fig. 103. Action of Sulphuric Acid on Zinc. Development of Heat Energy.

The inverse of this is likewise familiar. If we place in dilute sulphuric acid a stick of the metal zinc, we find that hydrogen is given off (Fig. 103), that the zinc goes into solution as zinc sulphate (p. 132), and that a large amount of heat is developed. The presence of small quantities of other metals in the zinc catalyzes this reaction. If impure zinc in fine particles, with much surface, is used, the temperature of the liquid may even rise spontaneously to the boiling-point. This form of the action produces heat. If, however, we attach the same stick of zinc to a copper wire and, having provided a plate of platinum also connected with a wire, immerse the two simultaneously in the acid (Fig. 104), then a galvanometer, with which the wires are

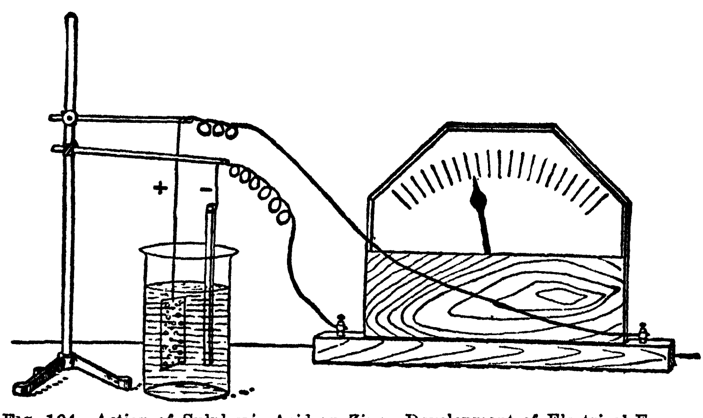


Fig. 104. Action of Sulphuric Acid on Zinc. Development of Electrical Energy.

connected, shows at once the passage of a current of electricity round the circuit. Exactly the same chemical change goes on as before. The sole difference is that the gas appears to arise from

the surface of the platinum. It is easy to show, however, that the platinum by itself is not acted upon by dilute acids and, in this case, undergoes no change whatever; it serves simply as a suitable conductor for the electricity. Here, then, in place of the heat which the first plan produced, we get an electric current. The arrangement is, in fact, a battery-cell, for a battery is a system in which a chemical action which would otherwise give heat furnishes electricity instead. Thus, **electrical energy may be consumed or produced** in connection with a change in composition.

Even **violent rubbing** in a mortar, in the case of some substances, can effect an appreciable amount of decomposition in a few minutes. In this way silver chloride can be separated into silver and chlorine, just as by light. It is the **mechanical energy** which is the agent, and part of it is *consumed* in producing the change, and only the balance appears as heat. Conversely, the *production* of mechanical energy, as the result of chemical change, is seen in the behavior of explosives and in the working of our muscles. Thus, **mechanical energy may be used up or produced** in chemical changes.

Summing up our experience, we may state that no change in composition occurs without some accompaniments, such as the production or consumption of thermal energy, radiant energy, electrical energy, or, in some cases, mechanical energy. It must be noted that **these phenomena are an essential part of the chemical change,** and are as important as is the production of new substances which goes on at the same time. We must, therefore, give attention to both.

The Practical Importance of Energy in Chemistry. — The absorption or liberation of energy accompanying a chemical transformation of matter is often, of the two, the more important feature. We do not burn coal in order to manufacture carbon dioxide gas. We are glad to get rid of the material product through the chimney. It is the heat we want. We do not buy gasoline (petrol) for an automobile in order to obtain various gases to expel through the muffler. We really pay for the mechanical energy. It is the same with burning illuminating-gas or magnesium powder when we want light, and with eating food, which we do, chiefly, to get energy to sustain our activity. We do not run electricity for hours into a storage battery, in order to make a particular compound (lead dioxide, for example), but in order to save and store the energy for future use. In industry and life fully half the total amount of chemical change involved is set in motion by us, solely on account

applicable in chemistry. Heat and electricity, for example, seem to be produced and consumed, in connection with changes in composition, in a mysterious manner. We trace light in an incandescent lamp back to the electricity, and this in turn to the mechanical energy, and this again to the heat in the engine. But what form of energy gave the heat developed by the combustion of the coal under the boiler, or by the union of iron and sulphur in our illustration (p. 22)? Since we do not perceive any electricity, light, heat, or motion in the original materials, and yet wish to create an harmonious system, we are bound to conceive of the iron and the sulphur, and the coal and the air, as containing another form of energy, which we call **chemical** or **internal energy.** Similarly, when heat is used up in decomposing mercuric oxide, or light in decomposing silver chloride, we regard the energy as passing into, and being stored in the products of decomposition in the form of internal energy.

These conclusions compel us, for the sake of consistency, to think of all our materials as repositories of energy as well as of matter, each of these two constituents being equally real and equally important. During the progress of a chemical change, like the union of iron and sulphur, the internal energy of the system also changes. The *total* energy which can thus be made available as the result of a chemical action **at constant temperature and pressure,** and converted (through, say, heat or electrical energy) into work, is called the **free energy** of the reaction.

It must be noted that the free energy, measured by work done, is *not,* in general, the equivalent of the heat developed by the natural progress of the change. Often the amounts are nearly equivalent, although never absolutely so. But frequently they are very different. When the free energy available for conversion into work is greater in amount than the heat of the reaction, as it often is, the difference is taken up from the heat of the surroundings during the progress of the change, and the vessels and objects in contact with the interacting bodies become colder. Thus phosphonium chloride (see p. 548) decomposes spontaneously into two gases, phosphine and hydrogen chloride, and ammonium carbonate gives off ammonia gas, while heat is absorbed in both cases. Work can be done by both these actions, although, so far as heat is concerned, not only is none of this form of energy liberated, but a certain amount of it is absorbed. Conversely, when the heat of reaction is greater than the equivalent of the free energy, then, along with the energy which could be used to do work (for example, by employing the action as a source of electricity), a certain amount of heat which cannot be transformed into work will be given to the surroundings. It thus appears that the substances which we handle are not only repositories of energy, but, when brought together, also play the part of machines for transforming energy which they take from or give to the surroundings.

Exothermal and Endothermal Changes. — The energy liberated in a chemical action appears most commonly in the form of heat. Changes which, like the union of iron and sulphur (p. 22), are accompanied by the liberation of heat are called **exothermal** actions. Those in connection with which heat is absorbed, like the decomposition of mercuric oxide (p. 23), are known as **endothermal.**

It should be noted here that neither the production nor the absorption of heat is an exclusive mark of chemical change. Physical changes are all likewise accompanied by the liberation or consumption of energy. Thus, water, in evaporating, absorbs heat, and liquids on solidifying, or often even when simply mixed with other liquids, give out heat.

Energy and Chemical Activity. — Other things being equal, when the free energy of a reaction is large, the reaction proceeds rapidly; that is to say, a large proportion of the reacting materials is changed in the unit of time. Those reactions in which the change of internal energy is small proceed more slowly. The speed of a chemical change, and the quantity of energy available because of it, are therefore closely related. Now, we are accustomed to speak of materials which, like iron and sulphur, interact rapidly and with liberation of much energy as "chemically active," or as possessing great "chemical affinity" for one another. Thus, **relative chemical activity** or *affinity* may be estimated:

1. By **observing the speed of a change** (see Speed of chemical actions, p. 141), or, in many cases,

2. By **measuring the heat developed** in the course of the action (see Thermochemistry, p. 260), or,

3. By **ascertaining the electromotive force of the current the change gives,** when arranged in the form of a battery-cell (see Electromotive series, p. 313). The *order of activity of the metals,* given on p. 142, is best obtained by this third method.

It is evident that the chemical activity or affinity of a given substance will not be the same towards all others. Thus, iron unites much more vigorously with chlorine than with sulphur and, with identical amounts of iron, more heat is liberated in the former case than in the latter. With silver, sodium, and many other substances, iron does not unite at all. One of the tasks of the chemist is to make such comparisons as this. He calls the results the *specific chemical properties* (see p. 87) of the substances in question. Evidently, the substances containing the most internal energy will be in general the most active.

Care must be observed, however, in making comparisons by the above methods. It should be noted here, first of all, that the speed of a given action may be enormously affected by conditions (see, for example, Catalysis,

p. 103), and that, therefore, great caution is required in inferring relative activities from observed differences in the speeds of several actions. Thermal measurements are also often misleading. This is evident from the fact that an action may be able to do work, even although heat energy is absorbed during its progress. Thus, ammonia at 1000° and under a pressure of one atmosphere decomposes of its own accord practically completely (see p. 507) into nitrogen and hydrogen, although it absorbs heat from surrounding objects in doing so. In the same way, although it is true that most chemical changes that take place readily *develop* heat, yet at high temperatures compounds can be formed by the direct union of their elements with *absorption* of heat (see, for example, p. 530). Reversible reactions (p. 177) must also be accounted for. In such reactions, one of the chemical changes taking place necessarily absorbs just as much heat as the other develops, yet both have a definite speed under any given conditions, as is shown by the fact that a fixed point of equilibrium is reached. Deacon's process (p. 238) is a good instance. As we shall see later (Chap. XVI), the relative *concentrations* of the reacting substances, as well as their *affinities*, must be taken into consideration.

The electrical method of measuring the available (free) energy, and therefore the true affinity, is in general the most trustworthy.

Thermochemistry. — As we have seen (p. 259) a chemical change may be accompanied either by a liberation or an absorption of heat. Actions, like the oxidations in Chapter VI, in which heat is produced, are called **exothermal** actions. Actions which, like the decomposition of mercuric oxide (p. 23), or of barium peroxide (p. 90), absorb heat, and proceed only so long as heat is furnished, are called **endothermal** actions. Since the activities or affinities of two substances (say, two metals) may often be measured (p. 264) by observing the amounts of heat liberated when each combines with a third substance (say, chlorine), it will be instructive now to consider some of the elementary facts of thermochemistry.

The chemical interactions to be studied thermally are arranged so that they may be carried out in some small vessel which can be placed inside another containing water. The heat developed raises the temperature of this water. The whole apparatus is called a **calorimeter** (Greek, *heat-measurer*).

Thermochemical Equations. — While in physics the unit of quantity is the gram, in chemistry the unit which we select is naturally a gram-atomic weight or a gram-molecular weight of the substance. Thus, the heat of combustion of carbon means the heat produced by combining twelve grams of carbon with thirty-two grams of oxygen, and is sufficient to raise nearly 100,000 grams of water one degree. This is expressed as follows:

$$C + O_2 \rightarrow CO_2 + 96{,}900 \text{ cal.}$$

In other words, the combustion of less than half an ounce of carbon will raise over two pounds of water from 0° to 100°.

When the action is one which absorbs heat, this fact is indicated by the negative sign preceding the number of calories. Thus for the dissociation of water vapor into hydrogen and oxygen we have the thermochemical equation:

$$2H_2O \rightarrow 2H_2 + O_2 - 116{,}200 \text{ cal.}$$

The *rate* at which a given chemical action is allowed to take place has no influence on the total amount of heat consumed or produced. It may not at first sight appear obvious that rusting evolves heat, but a delicate thermometer will show that a heap of rusting nails is somewhat higher in temperature than surrounding bodies. Poor conductors, like oily rags and ill-dried hay, show a tendency to spontaneous combustion owing to accumulation of the slowly developing heat of oxidation (p. 102). The warmth of our own bodies is due to the same cause.

Reversible Reactions. — In accordance with invariable experience (expressed in the law of the conservation of energy), when an action is chemically capable of reversal, the contribution of the same amount of heat which it develops will exactly suffice to drive the chemical change in the opposite direction. The heat contributed is simply used to restore the amount of chemical energy proper to the original system. Thus, the union of one atomic weight each of mercury and oxygen (p. 88) produces 30,600 cal.:

$$Hg + \tfrac{1}{2}O_2{}^{*} \leftrightarrows HgO + 30{,}600 \text{ cal.},$$

and the decomposition of one formula-weight of mercuric oxide (p. 23) demands the same amount of heat in order that free mercury and oxygen, with their appropriate proportions of internal energy, may be recovered.

In practice it is found that not all chemical changes are capable of reversal by the use of the sources of heat available in the laboratory. A quantity of heat, equivalent to that produced by any chemical action on a small scale, is very easily provided, but something more appears to be necessary. The heat must be provided at a certain *temperature*, otherwise it is quite ineffective. For example, the heat produced by the union of calcium and oxygen is within the limits of ready measurement,

$$Ca + \tfrac{1}{2}O_2 \rightarrow CaO + 131{,}000 \text{ cal.},$$

* Thermochemical equations are frequently written in this way, in order to avoid doubling the quantity of heat liberated (or absorbed) in the formation (or decomposition) of one formula-weight of a compound.

and the supply of this amount (or even of unlimited amounts) of heat to calcium oxide (quicklime) is easily achieved. Yet this method is quite ineffective to produce decomposition (p. 24) of the product. Apparently we have not sufficiently high temperatures for the purpose at our command (see Factors of energy).

It may be noted in this connection that the temperatures required to produce reasonably rapid decomposition vary within a wide range. Some substances can be kept only below 0°, and decompose when allowed to become warm. Others, like the oxides of gold and platinum, require a little heating (p. 143). Many, like quicklime, are not broken up even at the temperature of the electric arc. When the energy is applied in the form of electricity (p. 137), instead of heat, the range is incomparably more easily within the reach of the means ordinarily at our disposal. There is no substance, provided it is of such a nature as to be affected by the electric current at all, which cannot be decomposed by a current with an E.M.F. of 10 volts or less, while currents of 110 volts and over are commonly accessible. It is partly on this account that electrical processes have become so common in industrial chemistry.

Law of Constant Heat Summation. — One of the most important principles of thermochemistry is the **law of constant heat summation.** If a system of substances can be transformed into another system of substances by different stages or by more than one route, then the algebraic sum of the heats absorbed or produced in the various routes is the same. Thus, barium oxide might be formed either *directly* from the proper proportions of its constituents, or *indirectly* by preparing the peroxide (p. 90), and then driving out half of the oxygen contained in the latter. The quantities of heat involved in these two routes are as follows:

Direct: $Ba + \frac{1}{2}O_2 \rightarrow BaO + 124{,}400$ cal.

Indirect:

$$Ba + O_2 \rightarrow BaO_2 + 141{,}600 \text{ cal.} \qquad (1)$$

$$BaO_2 \rightarrow BaO + \frac{1}{2}O_2 - 17{,}200 \text{ cal.} \qquad (2)$$

$$Ba + \frac{1}{2}O_2 \rightarrow BaO + 124{,}400 \text{ cal.} \qquad (3)$$

When equations (1) and (2) are added algebraically, canceling terms which are common to both sides of the final equation (3), the fact that the indirect route is exactly equivalent to the direct one is at once apparent, and the balance, in favor of heat produced, is 124,400 calories as before. If in such cases the sum of the heats were not the same, it would follow that by using different plans of procedure we could prepare different specimens of the same substance containing different proportions of chemical energy. This, however, we have never been able to do.

The quantities of heat liberated in two chemical changes are often measures of the relative amounts of available chemical energy in the systems before the change, and, therefore, often furnish a measure of the relative chemical activities of the two sets of substances. The comparison may safely be made in certain cases when the conditions under which the two actions take place are precisely alike. Formerly it was supposed that the heat liberated was always proportional to the chemical activity of the substances, but we have already shown cause (pp. 258–60) why this general statement cannot be true.

The Cause of Chemical Activity or Affinity. — The reader will undoubtedly be inclined to inquire whether we can assign any cause for the tendency which substances have to undergo chemical change. Why do iron and sulphur unite to form ferrous sulphide, while other pairs of elements taken at random will frequently be found to have no effect upon one another under any circumstances? A final answer to this question cannot, of course, be given. As the facts regarding chemical activity or affinity, however, become better known, we may arrive at a stage where a logical *explanation* (see p. 34) can be advanced which, basing itself on these facts, affords a means of classifying them and supplies us with a new and useful hypothesis regarding matter in its various forms (iron, sulphur, etc.) and the energy contained therein. A brief discussion of such a hypothesis will be found in a later chapter (pp. 491–2); at this stage we shall confine ourselves to a few preliminary observations.

Attention has already been called several times to the fact that the atoms of most elements contain as an outermost shell a number of loose electrons. In the course of chemical reactions of the ordinary types which we have so far considered — such as combination, decomposition, and displacement — the interior part of each atom is entirely unaffected; only the outermost electrons change their positions. The atoms of certain elements commonly cast off all their loose electrons in entering into combination. The atoms of other elements take on extra electrons, while in certain cases pairs of electrons may be shared in common between two atoms. Now this shifting of electrons from their original arrangement entails a change in internal energy; work may be done or work may be expended in moving to the new stations.

The most important and at the same time the simplest type of reaction that we can examine in this connection is that of the combination of a typical metal, such as sodium, with a typical non-

metal, such as chlorine, to give a polar compound, such as common salt. The magnitude of the energy change here involved evidently depends upon two factors: (1) the tendency of the sodium atom to lose an electron, and (2) the tendency of the chlorine atom to gain an electron.* In this particular case the mutual tendencies are obviously quite strong, since their satisfaction leads to the formation of a very stable compound. Expressed quantitatively, the *heat of formation* of one gram-molecular weight of sodium chloride from its elements is 97,700 calories.

When other metals combine with chlorine, the heat of formation is different. The values for a representative series, expressed in calories per gram-equivalent weight (p. 153) in order to bring the results to a comparable basis — in other words, to obtain the heat of combination with 35.46 g. of chlorine throughout — are as follows:

Chloride	KCl	½$CaCl_2$	½$MgCl_2$	½$ZnCl_2$	½$PbCl_2$	AgCl	AuCl
Heat of formation	104,300	85,000	75,600	48,700	41,900	29,900	5,800

Comparison of these figures with the activity list of the metals (p. 142) will show that the heat of formation increases regularly as we proceed upwards in the table. Now the greater the heat of formation, the greater the loss in internal energy involved in the combination. The essential feature of the combination, in every case, is the transfer of electrons from the metal to the chlorine, so that we see that the energy change involved in this transfer is directly connected with the position of the metal in the activity series. To put the matter briefly, **the activity series represents the relative tendencies of the metals to lose electrons.** This is an important point to which we shall return later.

Exercises. — 1. Which form of energy is delivered as such, and paid for as such, in most cities?

2. How many calories are required to raise 500 g. of a substance of specific heat 0.5 from 15° to 37°?

3. The combustion of 1 g. of sulphur to sulphur dioxide develops 2220 calories. What is the heat of combustion of sulphur? Write the thermochemical equation.

* Strictly speaking, there is a third factor which also requires to be taken into consideration — the dissociation of the chlorine molecule into its component atoms. The significance of this *endothermic* stage of a reaction which, as a whole, is highly *exothermic* will be recognized in the discussion of a similar case (the production of ammonia from hydrogen and nitrogen) in a later chapter (p. 510).

either case a negative result is conclusive evidence of the absence of the radical tested for. If a positive result is obtained, the precipitate must be examined further, to prove whether or not it is silver chloride.

The appearance of a precipitate is *not*, however, an essential feature of a double decomposition (see the reaction between HCl and NaOH on p. 290). The most important point for us to notice is that, in all such reactions, each substance present behaves exactly as if it consisted of *two distinct radicals*. We may therefore regard double decompositions as a simple result of *the liberty of radicals to interchange partners*. In some cases, this exchange will be incomplete, and we obtain simply an *equilibrium mixture* (see p. 270). But because, in many systems, one of the four possible compounds *withdraws from the exchange of partners* by disappearing from the solution either as a gas (p. 225) or as a precipitate (p. 225) the reaction in such cases becomes practically complete in one direction (compare p. 282).

Another significant point may now be noted. Not only does every acid, base and salt in solution behave, in double decompositions, as if it consisted of *two distinct radicals*, but it can be shown to possess *two independent sets of properties*, one referring to each radical. Thus a solution of cupric chloride in water exhibits one set of properties which can be referred directly to the cupric radical, and which is accordingly not peculiar to cupric chloride, but is common to all cupric salts in aqueous solution. To mention only two of these: (1) the color of the solution, when diluted with water, is *blue*, and (2) the addition of a base gives a pale blue, gelatinous precipitate of *cupric hydroxide* (see equation (2) above). The same solution exhibits a second set of properties which can be referred directly to the chloride radical and which is consequently common to all chlorides. To mention only two of these again: (1) when the solution is heated with concentrated sulphuric acid, HCl is evolved (see p. 226), and (2) the addition of a silver salt gives a precipitate of *silver chloride*.

The properties of acids (p. 229) are properties of the *hydrogen radical* H. The properties of bases (p. 234) are properties of the *hydroxyl radical* OH.

A *radical*, then, is an *atom, or group of atoms, which behaves as a distinct unit in double decompositions, and which confers a definite independent set of properties upon solutions of all acids, bases or salts of which it forms one constituent.* Simple radicals also behave as separate units in *displacements*.

The distinct radicals, of whose existence we have thus become convinced, constitute a new set of materials (with appropriate names, see p. 305). Thus the hydrogen radical of acids, although a form of uncombined hydrogen, differs totally from the gas which is composed of the same element. The gas has no sour taste or effect upon litmus; these are properties of the free radical. The gas is very slightly soluble in water, while the hydrogen radical exists as a separate substance only in solution. Again, substances with the composition of the radicals NO_3 and SO_4 are not known at all except in solutions. The chief peculiarity of these substances is that a solution cannot be made which contains less than two kinds of them (one positive and one negative) side by side.

3. **Conductivity.** — Solutions of acids, bases, and salts in water are *all* conductors of electricity. Acids, bases, and salts are therefore called "electrolytes." *In all cases* the solution is decomposed

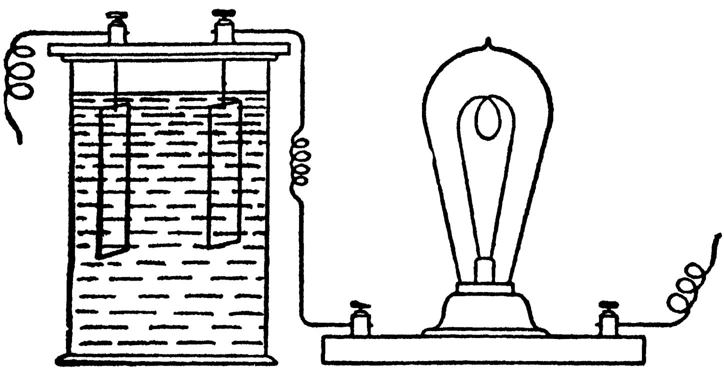


FIG. 106. Conductivity Demonstration.

by the passage of the current. The positive and negative radicals of which the solute is composed are attracted to the opposite electrodes. There, unless special circumstances prohibit (see, for example, the electrolysis of sodium chloride, p. 233), they are liberated. Thus, all acids give hydrogen at the negative pole, the other radical passing to the positive pole.

Of all the properties they have in common, this one of being electrolytes is perhaps the most remarkable. It appears more surprising when we consider that *no* substances, other than acids, bases, and salts, undergo electrolysis in aqueous solution. This is an exclusive property of these classes of bodies.

The conducting power of solutions can be examined, roughly, by the apparatus in Fig. 106. The platinum electrodes are connected with a direct-current circuit. The lamp, which is on one

of the wires, serves, by its resistance, to cut down the current. Its glowing also shows when the liquid is a conductor, and by varying brightness indicates roughly the conducting power of the solution.

A solution of sugar in water shows no conductance, and the lamp remains dark. Solutions of acids, bases, and salts in water enable the lamp to glow.

We quickly find that different solutions, when they conduct, do so in different degrees. Solutions of hydrochloric and nitric acids conduct well. So do solutions of sodium and potassium hydroxides. Salt solutions are practically *all* good conductors. But many acids, like acetic acid, conduct poorly in aqueous solution. The same is true of some bases, like ammonium hydroxide.

Substances which give solutions with high conducting power are called **strong electrolytes.** Substances which give relatively poorly conducting solutions are called **weak electrolytes.**

Of course, acids, bases, and salts which are only very slightly soluble in water give poorly conducting solutions. But in estimating the conductivity for chemical purposes, we have to take into consideration the amount dissolved. Thus silver chloride, being a salt, is an excellent conductor, when we allow for the extreme diluteness of the solution. A *saturated solution* of silver chloride, in point of fact, shows a slightly higher conductance than a solution of sodium chloride of the same concentration.

4. **Abnormal Vapor Pressures, Boiling-Points and Freezing-Points.** — We have seen (pp. 211–7) that equal numbers of molecules of different solutes dissolved in equal weights of water normally depress the vapor pressure, raise the boiling-point, and lower the freezing-point by constant amounts. Thus, one molecular weight of sugar (342 g.) or of glycerine (92 g.) dissolved in 1000 g. of water will raise the boiling-point from 100° to 100.52°, and will lower the freezing-point from 0° to — 1.86°. But this is uniformly true only of *non-conducting solutions,* in other words, solutions of substances which are not acids, bases, or salts. Gram-molecular weights of substances of these three classes, dissolved in 1000 g. of water, raise the boiling-point more than 0.52 degrees and lower the freezing-point by more than 1.86 degrees. We say they give *abnormal* elevations of the boiling-point and *abnormal* lowerings of the freezing-point. Vapor pressure depressions in such solutions are similarly *abnormal.*

Thus, a solution of 58.46 g. of sodium chloride in 1000 g. of water boils at 100.97°, and freezes at — 3.42°. The elevation in

the boiling-point of the water is 0.97° instead of 0.52°. The depression of the freezing-point is 3.42° instead of 1.86°. The effect in each case is *nearly twice* as great as the normal one. In the same way, a gram-molecular weight of potassium chloride dissolved in 1000 g. of water at 20° depresses the vapor pressure by 0.554 millimeter, while a gram-molecular weight of mannite (a simple sugar which gives a non-conducting solution) in the same amount of water lowers the vapor pressure by only 0.313 mm. Again the effect approaches twice the normal. In more dilute solutions it becomes almost exactly twice the normal.

The most natural conclusion we can draw from these results is that *twice the normal numbers of solute molecules are actually present* in such solutions, the deviations from strict proportionality at higher concentrations being due to deviations from the law of molecular concentration (compare pp. 278–9). In other words, not only do we have two independent sets of properties exhibited by the constituent radicals in solutions of electrolytes, but these same solutions apparently behave as if the radicals were altogether uncombined with each other. It appears as if sodium chloride, for example, is essentially *decomposed* (more strictly, *dissociated*) in aqueous solution into independent sodium and chloride radicals. Additional evidence in this direction is supplied by the behavior of electrolytes of more complex types, such as sodium sulphate Na_2SO_4 or zinc chloride $ZnCl_2$. Both of these substances, in dilute solution, give boiling-point and freezing-point changes which are nearly *three times* the normal, indicating that they are similarly dissociated into their three constituent radicals (2Na and SO_4; Zn and 2Cl). In the same way, substances containing four radicals, like ferric chloride $FeCl_3$, give effects approaching *four times* the normal in dilute solution.

One last point remains to be mentioned. It has been noted above that some acids, like acetic acid, and some bases, like ammonium hydroxide, are only poor conductors in solution. Just these same two classes of substances, it has been found, give only very slightly abnormal changes in the three physical properties of solutions here under examination. The full significance of this difference in behavior will appear in the following chapter.

A Warning. — The reader is urged to keep in mind the fact that it is *only in solution* (and particularly in *aqueous solution*) that the special properties of acids, bases, and salts become uniformly apparent. Their behavior is often quite different in the absence of a solvent. If, for example, we mix together dry ammonium carbonate $(NH_4)_2CO_3$ and partially dehydrated, solid cupric

nitrate $Cu(NO_3)_2$, and apply heat, a violent interaction begins. This interaction is nothing so simple as a double decomposition, however. An immense cloud of smoke and gas is thrown out of the tube, and the solid remaining is either black or reddish, in parts, according to the proportions of the substances employed. This residue contains black cupric oxide CuO, and sometimes red cuprous oxide Cu_2O. The gas evolved is tinged red by the presence of nitrogen tetroxide NO_2, while a careful analysis would show that it contained also carbon dioxide CO_2, nitrogen N_2, nitrous oxide N_2O, water vapor H_2O, and perhaps still other products.

The contrast, when the substances are dissolved in water before being brought in contact, is very great. A pale green precipitate is immediately produced, which rapidly settles out and proves, on examination, to be a carbonate of copper. Evaporation of the solution gives us ammonium nitrate:

$$(NH_4)_2CO_3 + Cu(NO_3)_2 \rightarrow CuCO_3\downarrow + 2NH_4NO_3.$$

The reaction is essentially a double decomposition (although, strictly speaking, the precipitate is not the normal carbonate of copper, but a *basic* salt $Cu_2(OH)_2CO_3$, see p. 291), similar in character to those already discussed.

The differences in properties between *dry hydrogen chloride* and *hydrochloric acid* (p. 229) furnish another good example of the fundamental changes involved in the addition of water as a solvent. Carefully dried hydrogen chloride has practically none of the properties of an acid. It does not affect litmus; it does not conduct the electric current. It is true that it does react with the more active metals (such as Na or K), hydrogen being displaced and the chloride of the metal formed. But it is probable that even this property would disappear if we could succeed in eliminating the last traces of moisture from our reacting products. A solution of *sulphuric acid* acts on sodium so vigorously that the mixture explodes, but pure *hydrogen sulphate* H_2SO_4, when very carefully dehydrated, is so inert that metallic sodium floats in it without the slightest evidence of any interaction.

Non-Electrolytes. — The aqueous solutions of some substances (chiefly compounds of carbon, such as sugar) do not conduct the electric current any better than water (see p. 295). Such substances are called **non-electrolytes.** Even although a non-electrolyte may contain hydrogen, hydroxyl, or other characteristic groups in its usually rather complex molecule, its solution exhibits none of the properties of acids, bases or salts developed in the preceding pages. Thus alcohol C_2H_5OH is *not* a base; nitroglycerine $C_3H_5(NO_3)_3$ is *not* a salt. The vapor-pressure depressions, boiling-point elevations and freezing-point lowerings obtained with such non-conducting solutions are never abnormally great. If any deviation is observed, it is always in the other direction, an abnormally small change suggesting that the substance may be partially *associated* in aqueous solution.

Substances which are typical non-electrolytes in aqueous solution correspond, in general, to those substances which retain molecu-

lar units as distinct groups in their crystal lattice structure (see p. 71) and which, in consequence of the lack of any definite electron transfer from one part of the molecule to another with the production of discrete positive and negative radicals, we have termed **non-polar compounds.** As such, they present entirely different chemical characteristics from those exhibited by typically polar compounds such as sodium chloride, which in aqueous solution function as **strong electrolytes.** It has been emphasized already, however (p. 149), that the distinction between polar and non-polar compounds is one of degree only, and that compounds of an intermediate type exist where the tendency towards electron transfer only partially prevails. If now we recognize the fact that these compounds of an intermediate type represent the class of **weak electrolytes,** we find ourselves in a position to offer a logical explanation for all of the phenomena which they exhibit. A brief introduction, however, is necessary.

Ions. — The unit particles in the crystal lattice of sodium chloride, a typical **polar compound,** are *not* (see p. 69) molecules of NaCl; the transfer of an electron from the positive radical Na to the negative radical Cl has led to the formation of a pattern which consists solely of sodium ions Na^+ and chloride ions Cl^-. In the crystal, these ions are bound in a rigid structure and are not free to move under the influence of an electric current. In solution, however, the rigid structure of the crystal is destroyed, and the particles of solute are dispersed throughout a much larger volume. The attractive forces between oppositely charged ions are thus considerably diminished, especially when the solvent is of such a nature (as it is in the case of water) that each ion becomes surrounded by an envelope of solvent molecules which shield it from its neighbors. Under such circumstances, it is easy to see that the ions may attain such independence of each other that they can be regarded as practically free. A solution of sodium chloride in water, therefore, contains no NaCl as such, but only Na^+ and Cl^-. The liberty of these two ions accounts for all of the properties exhibited by such a solution, its displacement reactions, double decompositions, conductivity, vapor pressure abnormalities, etc., as we shall show in detail later.

With non-electrolytes, on the other hand, such as sugar, molecular units persist in solution just as in the crystal; there is no breaking-up of molecules into positive and negative ions, they are simply dispersed throughout the solution as wholes. Compounds

of intermediate type, **weak electrolytes,** however, are more susceptible to changes of condition, such as solution. In molecules of such substances we have already a tendency for a loose electron to pass from one atom to another, and the dispersion of such molecules in a solvent such as water, which itself (see p. 318) is also a weak electrolyte tending to dissociate into hydrogen ion H^+ and hydroxyl ion OH^-, may be anticipated to facilitate such a transfer. Free ions will thus be produced in the solution, but we cannot expect dissociation in such a case to be complete, as in the case of NaCl. In a solution of acetic acid, for example, molecular $CH_3.COOH$ does not dissociate entirely into the ions $CH_3.COO^-$ and H^+, since whenever these two oppositely-charged ions collide, there is an opportunity afforded for the loose electron to return to its original location and for the molecular unit $CH_3.COOH$ to be re-established. Acetic acid, therefore, exists in aqueous solution partly in ionized and partly in molecular form, and the equilibrium between the two fractions may be expressed by the reversible reaction:

$$CH_3.COOH \rightleftarrows CH_3.COO^- + H^+.$$

Once more we must emphasize the fact that the distinction between polar and non-polar substances is not fundamental, but one of degree only. Strong electrolytes, weak electrolytes and non-electrolytes, consequently, are not rigidly separable; each class merges into the other and the same substance even, under different conditions, may change its position in the scale. Thus HCl in water solution is a strong electrolyte, but dissolved in 100% sulphuric acid H_2SO_4 (see p. 226), it is a very weak electrolyte. Water, on the other hand, is usually regarded as an exceedingly weak electrolyte, since pure water conducts the electric current very poorly, but dissolved in 100% sulphuric acid water appears as a strong electrolyte!

Bearing this in mind, we shall find it most convenient, in considering the behavior of electrolytes in general, to take up the intermediate case of weak electrolytes in greatest detail. From the results of our study of the general equilibrium $RX \rightleftarrows R^+ + X^-$ we can then readily extend our conclusions to the limiting case where RX becomes negligible (in strong electrolytes). This procedure will have the additional advantage of following the historical development of the subject closely. As a matter of fact, even a substance like hydrogen chloride is conceded to possess a measurable fraction of undissociated molecules in concentrated aqueous solution, so that our preliminary treatment of ionization as an incomplete process may be extenuated as partially applicable, indeed, even to many so-called typical strong electrolytes.

Some Possible Misunderstandings. — Before we close the chapter, it will be profitable to anticipate some difficulties into which the reader may fall. The following points of possible misunderstanding and the explanations appended should therefore be read

through very carefully. For convenience of illustration, *sodium chloride* is taken as a typical electrolyte in the questions and answers listed below. The student should test his knowledge of the subject by substituting other electrolytes.

1. If sodium chloride is broken up in aqueous solution into *sodium* and *chlorine,* why do we not find any of the properties of sodium or of chlorine exhibited by the solution? — This has always been a very common misapprehension of the ionic theory. Many prominent chemists never could understand how sodium (a *metal* which acts vigorously on water) and chlorine (an obnoxious *gas*) could exist side by side in a solution of sodium chloride without immediately notifying us of their presence by characteristic reactions. The answer is that *free sodium* and *free chlorine* do *not* exist in sodium chloride solution. The ionic hypothesis has never stated that they do. What it does state is that *sodium-ion* Na^+ and *chloride-ion* Cl^- are present in the solution. These are *entirely different substances* from atomic sodium Na and molecular chlorine Cl_2. There is no more reason why they should behave like free sodium and free chlorine than there is for crystals of common salt to behave like a *mixture* of sodium and of chlorine. Metallic sodium Na reacts with water to form a solution of sodium hydroxide. In sodium chloride solution, however, the ionic sodium Na^+ is *already* in the same state as it is in sodium hydroxide solution, and is in no need of trying to enter that state.

2. Salt is a very stable substance. The union of sodium and chlorine evolves a great deal of heat (p. 264). A great deal of work will be required, therefore, to decompose sodium chloride. How can mere addition of water break it up? — We have here the same misunderstanding in another form. It is true that it would be very difficult to decompose sodium chloride into *free sodium* and *free chlorine,* but its dissociation into *free sodium-ion* and *free chloride-ion* (as may be gathered from the discussion on p. 298) is an entirely different question.

3. Why do not the ions Na^+ and Cl^- *recombine at once,* in response to the attractions of their charges? — The answer is that they do *tend* to combine. The tendency towards combination is, however, completely eclipsed by the tendency of sodium chloride in aqueous solution to decompose into *free ions.* With less polar substances, an observable equilibrium between the two tendencies is, nevertheless, set up, which we may express, for convenience, by the general reversible reaction $RX \rightleftarrows R^+ + X^-$ (p. 299).

4. Why can we not separate sodium ions from chloride ions in

a solution of sodium chloride *before* we pass a current through the solution? Does not this show that it is the electric current which breaks up the sodium chloride? — The charges on the ions are *not* derived from the electric current. Free sodium ions and free chloride ions are present in the solution the instant the salt is dissolved, whether a current is passing or not. Before we pass a current through the solution, however, any portion of it of sensible magnitude contains just as many sodium ions as chloride ions. By making use of the fact that chloride-ion *diffuses* more rapidly than sodium-ion (into a layer of pure water, for example, carefully poured over the solution) we can bring about a minute separation of the two ions, the water layer becoming negatively charged and the solution positively. The passage of the current does not *cause* ionization, it merely makes its existence more obvious, effectually separating the ions by forcing them to migrate in different directions toward the oppositely-charged electrodes. We shall return to this question in greater detail in the following chapter.

Exercises. — 1. By what experiments should you determine which were the radicals in substances of the following composition:

$Cu(NO_3)_2$, $CaCO_3$, NH_4Br, NH_4I, $KClO_4$ and $KMnO_4$?

There are always two ways, and usually three, of determining the radicals — what are they (pp. 291–4)?

2. How should you determine whether a given substance were an acid, a base, a salt, or a non-electrolyte?

3. Make equations showing the interactions of solutions of aluminium chloride $AlCl_3$ and of cupric sulphate $CuSO_4$ with sodium hydroxide (p. 234). Name the products.

4. Make equations showing the interactions of solutions of zinc chloride $ZnCl_2$ and of ferric chloride $FeCl_3$ with silver sulphate Ag_2SO_4. Name the products.

5. What is the action of metallic zinc on solutions of sodium chloride, lead nitrate $Pb(NO_3)_2$, silver sulphate Ag_2SO_4, magnesium sulphate $MgSO_4$, mercuric chloride $HgCl_2$?

6. From a study of the solubility data on the inside front cover, devise preliminary tests for the presence of the following radicals in a given solution: calcium, magnesium, lead, bromide, iodide, oxalate (C_2O_4).

7. Dilute solutions of potassium chromate K_2CrO_4 and of chromic chloride $CrCl_3$ are taken in different test-tubes. To each a few drops of barium chloride solution are added. Why do the two solutions give different reactions? Formulate what occurs in each case.

8. Methyl chloride CH_3Cl and trichloracetic acid CCl_3COOH both fail to give a precipitate with silver nitrate solution. What do you conclude?

CHAPTER XVIII

THE IONIZATION THEORY OF ARRHENIUS

It was established many years ago by careful experiment that electrolytic solutions obey Ohm's law just as rigorously as do metallic conductors, the current passing being directly proportional to the electromotive force, even for very small values of the latter.* From this fact, it must follow that no electrical energy is expended in breaking up the molecules of the solute into their constituent ions, and therefore the solution must contain *some* free ions, whether a current is passing through it or not. It was assumed by Clausius, however, that the proportion of dissociated solute was in all cases immeasurably small, the free ions removed at the electrodes being regenerated continuously by collisions of the undissociated molecules during the process of electrolysis.

This was the universal view until 1887, when a young Swedish chemist, Svante Arrhenius, first definitely advanced a new ionization hypothesis which postulated that solutes of high conducting power were very extensively dissociated. In spite of considerable opposition at the start, this hypothesis was found to explain so many hitherto inexplicable facts that it has become the basis of modern electrochemical theory. An outline of its main features and of some of its elementary consequences is presented in the following sections.

The results of recent researches — it must be frankly conceded — have thrown an entirely new light upon certain long-standing points of difficulty in the Arrhenius ionization theory, and have led us to the conclusion that, for the most important class of conducting solutes (the so-called strong electrolytes, see p. 299) the theory as originally developed is in need of drastic modification. A similar fate, it will be remembered, has overtaken several other basic chemical principles in late years, *e.g.*, the law of definite proportions (p. 42) and Dalton's atomic theory (p. 69). Nevertheless, since it is impossible for the beginner to understand why certain features of any theory must be recast until that theory has first of all been developed for him in detail as simply as possible, we shall defer a full discussion of the new ideas which have been in-

* It is essential that polarization effects at the electrodes should be rigorously avoided (see p. 310).

jected into the ionization hypothesis, important though they be in their consequences, until we are prepared to apply them properly. Where there are significant discrepancies between the classical theory and the experimental facts, attention will be called thereto, but it would be just as inconsistent, in the present state of our knowledge, to begin the discussion of ionization with an account of these discrepancies as it would be to start to consider the behavior of gases by enumerating the deviations from the laws of Boyle and of Charles, without making the student thoroughly familiar with these two laws in advance. Accordingly, when the expert in the field finds certain statements in the following pages which appear to him to be not in strict accordance with the most modern view-point, he is requested to recognize that his less advanced fellows must learn to walk before they can run, and that the necessary modifications to these statements will in most cases be clearly indicated at appropriate points later on in the volume.

The Ionic Hypothesis. — In this hypothesis of Arrhenius we start with the assumption that a significant proportion (indicated, as we shall see later, by the conductivity) of the molecules of an electrolyte RX are broken up in solution into their constituent radicals R^+ and X^-, *each radical being electrically charged.* These charged radicals have been called *ions,* and the hypothesis is hence known as the **ionic hypothesis.**

Of course there is assumed to be, under the theory of Arrhenius, an equilibrium between the undissociated and dissociated parts of an electrolyte in solution, and this equilibrium may be represented by the ionic equation:

$$RX \rightleftarrows R^+ + X^-.$$

The varying extent of the ionization with different electrolytes may be conveniently indicated by modifying the thickness of the arrows. Thus for hydrochloric acid and acetic acid, respectively, we have the equilibria:

$$HCl \rightleftarrows H^+ + Cl^-; CH_3.COOH \rightleftarrows H^+ + CH_3.COO^-.$$

A solution of hydrogen chloride in water is supposed therefore, according to this hypothesis, to consist of two parts: (1) an undissociated part, made up of hydrogen chloride molecules HCl; (2) a dissociated or ionized part, made up of equal numbers of hydrogen atoms which have lost an electron (H^+) and chlorine atoms which have gained an electron (Cl^-). That small portion of the hydrogen chloride remaining undissociated in solution is understood to be *inactive.* It plays no part in the conduction of the current, it exerts a normal effect on the physical properties of the solution (vapor pressure, boiling-point and freezing-point changes), it does not convey to the solution any of the properties of an *acid,* it takes no direct share in displacements or double decompositions. That much larger portion of the hydrogen

chloride, on the other hand, which breaks up into hydrogen-ion H^+ and chloride-ion Cl^- is understood to be *active*. All of the special properties of the solution may therefore be referred to these ions, as we shall see below.

Since the solution, as a whole, has itself no charge, **equal quantities of positive and negative electricity must be produced.** This means that bivalent radicals, on dissociation, will become ions carrying a double charge and trivalent ions must carry a triple charge:

$$CuCl_2 \rightleftarrows Cu^{++} + 2Cl^- \qquad CuSO_4 \rightleftarrows Cu^{++} + SO_4^{=}$$
$$HgCl_2 \rightleftarrows Hg^{++} + 2Cl^- \qquad FeCl_3 \rightleftarrows Fe^{+++} + 3Cl^-$$

In these equations, the coefficients multiply the charges as well as the radicals bearing the charges, and it will be seen that the numbers of positive and negative charges produced by each dissociation are equal. Hence, **univalent ions all possess equal quantities of electricity, and other ions bear quantities greater than this in proportion to their valence.** This is an inevitable inference from the electrical neutrality of all solutions. An **ion** is therefore **an atom or group of atoms bearing an electric charge, or a number of such charges.** In modern terminology, a **positive ion** is a free atom, or a group of atoms, which has **lost** an electron, or a number of electrons, such as Na^+, $(NH_4)^+$, Zn^{++}. A **negative ion** is a free atom, or a group of atoms, which has **gained** an electron, or a number of electrons, such as Cl^-, $(NO_3)^-$, $S^=$.

The positive ions are called the **cations,** since they move toward the negative electrode, or cathode. The negative ions are the **anions,** and move toward the positive electrode, or anode.

It must be mentioned that ionization is not restricted to solutions of electrolytes in *water*. Many other solvents, such as liquid ammonia NH_3, formic acid H.COOH, ethyl alcohol C_2H_5OH, dissolve many electrolytes to give solutions of excellent conducting power. Water, however, is the solvent most commonly used in chemical operations, and other ionizing solvents need not be considered at this stage.

The solvents which produce ionization are all associated liquids (p. 357). Those which do not produce ionization are the non-associated liquids like benzene, toluene, and carbon disulphide. This likewise is explained by the fact that the former have, by measurement, high *dielectric constants,* and so are able to hold charged bodies apart, while the latter have low ones.

The **dielectric constant** of a solvent medium, it should be noted, is the property which determines the magnitude of the forces between electrically charged particles existing in that medium. The higher the dielectric constant, the smaller the attractive forces exerted between particles of opposite charge. For further details, a text-book on physics should be consulted.

Nomenclature. — Since ionic hydrogen, ionic chlorine, etc., are entirely different in physical and chemical properties from the corresponding free elements, they should receive separate **names.** Since it is inconvenient to say "ionic hydrogen," "ionic nitrate radical" (NO_3^-), etc., the following representative **names** will be used for the **ionic substances:**

Symbol	Name of Substance	Anion of	Symbol	Name of Substance	Cation of Salts of
$SO_4^{=}$	Sulphate-ion	Sulphates	Na^+	Sodium-ion	Sodium
Cl^-	Chloride-ion	Chlorides	Fe^{+++}	Ferric-ion	Ferric iron
HSO_4^-	Hydrosulphate-ion	Bisulphates	NH_4^+	Ammonium-ion	Ammonium
OH^-	Hydroxyl-ion	Hydroxides (bases)	Fe^{++}	Ferrous-ion	Ferrous iron
			H^+	Hydrogen-ion	Hydrogen (acids)

Actual Quantities of Electricity Concerned. — In a preceding paragraph we reached the conclusion that univalent ions all possess equal quantities of electricity, and other ions bear quantities greater than this in proportion to their valence. This conclusion is confirmed by actual measurement. When hydrochloric acid is electrolyzed, 35.46 g. (= Cl) of chlorine are liberated for every 1.008 g. (= H) of hydrogen. But when cupric chloride $CuCl_2$ is substituted, for every 35.46 g. (= Cl) of chlorine set free, only 31.78 g. ($= \frac{1}{2}$ Cu $= \frac{1}{2} \times 63.57$) of copper is deposited. The **law,** discovered by **Faraday,** is that **equal quantities of electricity discharge equivalent quantities of the ions** (equivalent, p. 153, *not* atomic or molecular).

The units of electrical energy are the **coulomb,** which is the unit of quantity, and the **volt,** which is the unit of intensity, or potential difference between the electrodes (*electromotive force*). Faraday's law has to do only with the former. Equal numbers of coulombs liberate equivalent weights of all elements, but different voltages are required to decompose different compounds, according to their stability (see p. 848).

To liberate 1.008 g. of hydrogen, or one equivalent of any other element, 96,500 coulombs of electricity are needed. The charges on 1.008 g. of hydrogen ions must, therefore, equal this amount. A simple calculation shows therefore (refer to p. 73) that each coulomb is distributed over about 63×10^{17} univalent ions.

A current of 1 coulomb per second is called 1 **ampere.** Thus, the current passing through a 1-ampere lamp will liberate 1.008 g. (11.2 liters) of hydrogen in 96,500 seconds, or 26 hours and 48 minutes. The same current will liberate 107.88 g. of silver (Ag^I)

from silver nitrate, or 31.78 g. of copper ($Cu^{II}/2$) from cupric sulphate in the same time.

The passage of equal quantities of electricity through several different acids liberates equal amounts of hydrogen from each. This is true, whether the passage of the given quantity of electricity is compressed into a brief time in one case and spread over a longer time in another, or is uniform in all cases compared. It is irrespective of the state of dilution and of the temperature of each acid. Thus two moles of hydrochloric acid HCl are always decomposed for every one of sulphuric acid H_2SO_4 by the same current. Similarly, if in different cells we place solutions of substances like sodium chloride NaCl, cupric chloride $CuCl_2$, antimony chloride $SbCl_3$, ferrous chloride $FeCl_2$, and ferric chloride $FeCl_3$, equal amounts of chlorine are liberated by currents of equal strength in the same time in each.

If we consider the relation of these facts to the equivalence of the

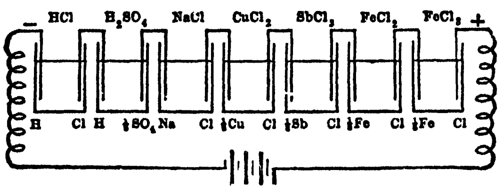


FIG. 107. Experiment to illustrate Faraday's Law.

materials liberated in any one cell, it will be evident that when one gram of hydrogen is liberated from each of the two acids mentioned above, one equivalent of chlorine will be set free in the one cell, and one equivalent of SO_4, or half the weight represented by the formula, will be set free in the other. Similarly, with the chlorides of the second and third metals, while 35.46 g. of chlorine are being liberated in each cell, the quantities of the metal set free will be, of copper one-half of 63.57 g., and of antimony one-third of 121.77 g. Finally, with the two iron salts, the quantities of iron liberated by the same current will be one-half and one-third of 55.84 grams, respectively.

The simplest way in which to insure the passage of precisely equal amounts of electricity through all the cells is to arrange them in series. We know that in such circumstances the quantity of electricity traversing any section of the whole circuit must be the same as that traversing any other. In a series of cells containing substances like the above, therefore, during the time that

1.008 g. of hydrogen is being set free, we shall have liberation of the equivalent quantities of each of the other ions (Fig. 107). Even in the *battery* which generates the current, the chemical changes taking place proceed in unison with those in the cells on the circuit. For example, if the battery contains zinc plates, for every atom of zinc that dissolves, one of copper and two of chlorine will be liberated in one of the cells. Our imagined mechanism thus puts all the processes going on in the circuit in the light of movements of the parts of a perfectly adjusted and interlocked machine.

Ions and Electrolysis. — We have already presented (p. 136) the primary features of the phenomena of electrolysis of an acid. The problem may now be more generally discussed. A solution of RX in water is assumed to contain three kinds of solute; undissociated RX molecules, positively charged ions R^+, and negatively charged ions X^-. These are scattered indiscriminately throughout

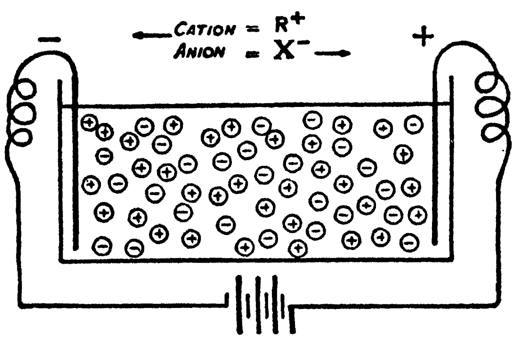


FIG. 108. Electrolysis (diagrammatic).

the solution, as indicated in Fig. 108 (only the two ions are there shown, the undissociated part is omitted since it plays no direct part in the electrolysis). Equilibrium is kept up by continual dissociation and recombination, according to the equation $RX \rightleftarrows R^+ + X^-$.

As soon as the circuit is completed, all the ions in the solution begin to *migrate* towards their proper electrodes. The positively-charged ions R^+ are attracted towards the negative electrode, the negatively-charged ions X^- are attracted towards the positive electrode. On reaching the electrode the ions may simply be discharged, or secondary reactions may occur (see below). Meanwhile, in the body of the solution, the departure of the ions has disturbed the equilibrium $RX \rightleftarrows R^+ + X^-$. Any undissociated RX consequently continues to break up, attempting to reëstablish equilibrium, until the electrolysis is complete.

By electrolysis of a solution of hydrochloric acid, in this way (see p. 136), we obtained hydrogen and chlorine. A substance thus directly set free is called a **primary product** of the electrolysis. In the foregoing instance both products are primary. With some electrolytes the course of events is not so simple, secondary reactions taking place at the electrodes. Thus when we pass a current through a solution of sodium chloride, we obtain chlorine at the positive electrode, but hydrogen instead of sodium is liberated at the negative electrode (see p. 233). Similarly, when we electrolyze a solution of a base, such as sodium hydroxide, oxygen is always liberated at the *positive* electrode. This is due to the decomposition of the hydroxyl radical OH, which cannot exist in the free state:

$$4OH \rightarrow O_2 + 2H_2O.$$

Here the oxygen is a **secondary product** of the electrolysis. In the same way, when we electrolyze a solution of cupric sulphate, metallic copper is deposited on the negative electrode, but the radical SO_4 cannot exist in the free state, and reacts with the water present to liberate oxygen, according to the equation:

$$2SO_4 + 2H_2O \rightarrow 2H_2SO_4 + O_2.^*$$

All acids give hydrogen alone at the negative electrode, whatever may be the product at the positive. All bases give oxygen alone at the positive electrode, whatever may be the product at the negative.

Even when we do not actually isolate the free radicals of an electrolyte by electrolysis, however, we can show that they have migrated with the current in the usual way by the fact that they collect around the electrodes. Thus, in the electrolysis of sodium chloride, the solution around the negative electrode becomes *alkaline,* owing to accumulation of sodium hydroxide. Similarly, in the electrolysis of copper sulphate, the solution around the positive electrode becomes *acid,* owing to accumulation of sulphuric acid.

* For the electrolysis of sulphate solutions as carried out in actual practice, the above equation is essentially correct. Theoretically, however, the possibility exists of the electrical energy discharging a less active negative radical (hydroxyl OH), in just the same way as hydrogen is liberated in preference to sodium in the electrolysis of a solution of sodium chloride (p. 233). This action undoubtedly takes place to some extent, but plays only a very minor part in ordinary cases. A more extended and critical discussion of the electrolysis of sulphate solutions is given on p. 853.

The Electrical Energy Required to Decompose Different Compounds. — Chemical compounds are of very different degrees of stability, and hence the quantities of energy, electrical or otherwise, required to decompose them vary widely. Thus, hydrogen chloride is very stable, while hydrogen iodide is easily decomposed by heating. The separation of the free elements from one mole (equivalent quantities) of these substances in aqueous solution absorbs 39,300 cal. and 13,100 cal. of heat energy, respectively. Hence, although equal quantities of electricity (96,500 coulombs in each case) perform this office, very unequal amounts of electrical energy are used up in the electrolysis.

The energy in a stream of water is represented by the product of the quantity passing a given section and the pressure or head of water available at that point. If the pressure is low, the work that can be done will be small, even if the quantity flowing is great. So electrical energy is expressed by the product of the current strength, or quantity of electricity passing per second during a certain period of time, and the electromotive force. The latter corresponds to pressure, and is defined by the difference in potential of two points in the circuit between which the energy is being used up.

Now, in the series of cells which was described (p. 306), each cell, while being traversed by the same quantity of electricity as any of the others, cuts down the electromotive force of the current in proportion to the amount of energy consumed by the decomposition going on within it. Hence, while a voltmeter will show no difference in potential between two neighboring parts of the heavy wires used as connections, for practically no resistance to the current is offered in the wires, it will show a considerable difference in potential between two points which are separated by one of the cells.

We should infer from this, that to decompose every electrolyte, a current of a certain minimum electromotive force, sufficient to furnish the fall in potential necessitated by the chemical change, which would be different in different cases, would be required. This is found to be the case. For the easy decomposition of sulphuric acid and liberation of the products an electromotive force of at least 1.96 volts is necessary, for hydrochloric acid 1.35 volts, for hydriodic acid 0.62 volt, for zinc sulphate 2.7 volts, and for silver nitrate 0.70 volt. When we use a current of electromotive force falling short of that specified, we find that the flow of electricity is interrupted.

The electrolytic cell practically forms a break in the circuit (see Chap. XLIX).

Polarization. — It is found that when plates of platinum, a metal which is not acted upon by the liberated radicals, are used, the products of electrolysis accumulate on the electrodes and tend to produce a reverse, or polarization, current (see p. 848). The cell is said to be **polarized.** Thus, after hydrochloric acid has been electrolyzed for a few moments, hydrogen and chlorine adhering to the two platinum plates set up this reverse current.* If the battery is disconnected, the electrolytic cell becomes for a brief time itself a battery, the re-ionization of the hydrogen and chlorine (reproducing hydrochloric acid) furnishing the energy. It is the continuous overcoming of this reverse current, and prevention of the re-ionization, that demands the minimum electromotive force (here 1.35 volts) of which mention has just been made.

It is possible to arrange cells in which no polarization can take place. Thus, when we electrolyze cupric sulphate between *copper* electrodes, the copper is deposited upon one plate and the SO_4 removes the copper from the other plate, forming cupric sulphate, thus restoring the electrolyte to its original condition. The only difference is that a portion of the copper has been deposited on one pole and an equivalent amount has been removed from the other (see Copper refining). With such cells, no minimum difference in potential is required to effect electrolysis, for there is no polarization current to be overcome. The feeblest electric current will produce continuous, if slow, chemical change.

This result is extremely interesting, for it shows that the operation of migration in itself does not require the consumption of much energy. If the molecules were actually torn apart by the electricity, then all electrolytic operations would require a minimum electromotive force for their maintenance. The fact just stated, therefore, is significant, for it confirms the present views in regard to the theory of solutions. This fact is in agreement with the belief that the actual production of the ions is accomplished in the solution in advance, and quite independently of the use of electricity, and that the sole function of the electricity in the process of electrolysis *within the solution* consists in the pilotage of the ions in reverse directions according to their charges, an operation which necessarily consumes but little energy. The friction alone of the moving ions has to be overcome. It makes clear the fact that it is only when the chemical change in the cell involves the actual decomposition of some material, accompanied (as in the electrolysis of hydrochloric acid) by the final delivery of the constituents in the free state,

*If copper plates are used, cupric chloride is formed at the positive plate (anode), and no polarization can occur at that plate.

that considerable consumption of electrical energy, proportional to the extent of the chemical change, must take place.

Ionic Migration. — A very convenient arrangement for observing the migration of ions is to dissolve copper sulphate in warm water containing about 5 per cent of agar-agar (a gelatine obtained in China from certain sea-weeds), and to fill with this mixture the lower part of a U-tube (Fig. 109). The setting of the jelly prevents subsequent mixing with the rest of the filling of the tube, and the consequent disappearance of the boundary of the blue solution. A few grains of charcoal are scattered on the surface of the jelly to mark the initial position of this boundary in each limb, and a warm solution of some colorless electrolyte, such as potassium nitrate, also containing agar-agar, is added on each side. When this has set, a little potassium nitrate solution in pure water is also added on each side, and in this the electrodes are inserted. The whole is finally placed in ice and water, to prevent melting of the jelly by the heat caused by resistance, and the current is then turned on.

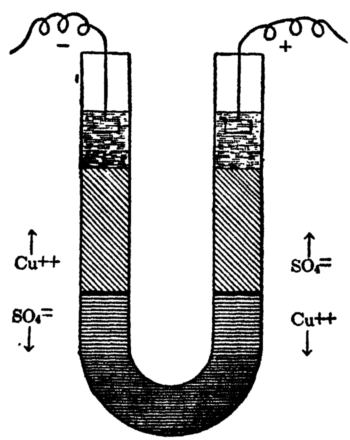


FIG. 109. Ionic Migration.

After a time, we observe that the blue cupric ions ascend above the mark on the negative and descend away from it on the positive side. In each case there is no shading off in the tint. The motion of the whole aggregate of colored cations occurs in such a way that, if the contents of the tube were not held in place by the jelly, we should believe that a gradual transference of the entire blue solution was being observed. With a current of 110 volts, and a 16-candlepower (one-half ampere) lamp in series with the cell, the effect becomes apparent in a few minutes.

Although the sulphate ions are invisible, we may safely infer that they are drifting towards the positive electrode. Indeed, this can be demonstrated by interposing a shallow layer of jelly containing some barium salt a little distance above the charcoal layer on the positive side. When the sulphate ions reach this, barium sulphate $BaSO_4$ begins to be precipitated and the layer becomes cloudy. In similar ways the progress of other colorless ions may be rendered visible.

It is evident, therefore, that electrolysis is not a local phenomenon, going on round the electrodes only, but that the **whole of the products of the dissociation of the solute are set in motion.**

Different ions move with different speeds. Under comparable conditions, the hydrogen ion is the most speedy, the hydroxyl ion comes next (see p. 315). The speeds of all ions are individual *properties and are independent of the nature of other ions that may be present, but are directly proportional to the rate of fall of potential* between the positive and negative electrodes.

By an experiment similar to the last, and devised by A. A. Noyes, the relative speeds of different ions may be demonstrated. The U-tube (Fig. 110, showing the same tube *A* before the current starts, and *B* after it has been passing for some time) is partly filled with agar-agar jelly containing potassium chloride and phenolphthalein. On the right side, a drop of potassium

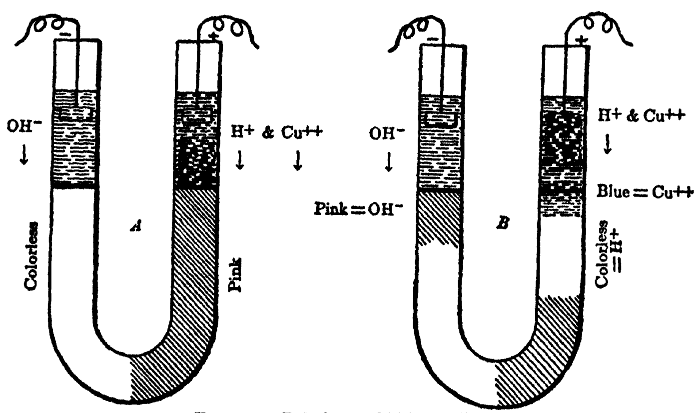


FIG. 110. Relative Mobilities of Ions.

hydroxide has been added to render the mixture pink. On the left, a drop of hydrochloric acid is present, and the mixture is colorless. Above the charcoal layer, in the right limb, a mixture of hydrochloric acid and cupric chloride, and in the left limb potassium hydroxide solution, are placed. The positive electrode is introduced on the right and the negative on the left. The hydrogen and copper ions drift away from the positive and towards the negative electrode, the hydroxyl ions away from the negative and towards the positive electrode. The motion of the H^+ is marked by the disappearance of the pink color, that of the Cu^{++} by the advance of a blue layer, that of the OH^- by the progress of a pink coloration (see p. 235). By the time the hydrogen ions have been displaced 5½ cm., the copper ions have moved 1 cm. and the hydroxyl ions about 2½ cm. These distances indicate their relative *speeds of migration.*

Ions and Displacement.—When a metal acts upon a dilute acid, and hydrogen is liberated, it is the ions alone that are directly concerned in the mechanism of the action. Thus the equation for the action of zinc on hydrochloric acid may be written:

ELECTROMOTIVE SERIES OF THE METALS.

Potassium
Sodium
Barium
Calcium
Magnesium
Aluminium
Manganese
Zinc
Chromium
Iron
Cadmium
Cobalt
Nickel
Tin
Lead
Hydrogen
Antimony
Bismuth
Arsenic
Copper
Mercury
Silver
Platinum
Gold

$$Zn + 2H^{+} + 2Cl^{-} \rightarrow Zn^{++} + 2Cl^{-} + H_2 \uparrow$$

or:

$$Zn + 2H^{+} \rightarrow Zn^{++} + H_2 \uparrow .$$

Similarly the action of zinc on a solution of a copper salt may now be written:

$$Zn + Cu^{++} \rightarrow Zn^{++} + Cu \downarrow .$$

All the metals, indeed, can be set down in an order, such that each metal displaces those following it in the list and is displaced by those preceding it. This list is known as the **electromotive series** of the metals, because in electrolysis of solutions containing normal concentrations of these ions, the electromotive force of the current required to deposit each metal is less than that for the metal preceding in the list (see p. 846). For present purposes, the list shows the metals in **the order of diminishing tendency to enter the ionic from the elementary condition.** In other words, **it represents the order of the tendency of the free elements to lose electrons.** The higher a metal stands in the series, the more readily will its atoms assume the ionic state by transference of electrons to positive ions of metals lower down in the series. If we represent an **equivalent of electrons** (the quantity of electricity carried by one equivalent of a negative ion) by Θ, therefore, we can write the action of zinc on a solution of a copper salt as the result of two distinct reactions:

$$Zn \rightarrow Zn^{++} + 2\Theta;\; 2\Theta + Cu^{++} \rightarrow Cu.$$

Similarly for the action of aluminium on hydrochloric acid:

$$2Al \rightarrow 2Al^{+++} + 6\Theta;\; 6\Theta + 6H^{+} \rightarrow 3H_2.$$

The electromotive series embodies many facts in the behavior of the metals, and should be kept in mind as **furnishing a key to all actions involving solutions in which a free metal is used or produced.** It is, in fact, identical with the order of activity (p. 142).

Similarly, among the non-metals or negative elements, fluorine displaces chlorine from chloride-ion, chlorine displaces bromine from bromide-ion:

$$Cl_2 + 2Br^- \rightarrow 2Cl^- + Br_2,$$

and bromine displaces iodine from iodide-ion (p. 354). Each of these actions, like those for positive ions given above, is independent of the nature of the other ion which accompanies the one undergoing change.

Ions and Double Decomposition.—The mechanism of reactions of this type also becomes much clearer when we write the equations in the ionic form. Thus, for the precipitation of silver chloride by the action of hydrochloric acid on silver nitrate solution, we have (according to the Arrhenius theory):

$$\begin{array}{rcl} AgNO_3 & \rightleftarrows & Ag^+ \quad + \quad NO_3^- \\ HCl & \rightleftarrows & Cl^- \quad + \quad H^+ \\ & & \upharpoonleft\downharpoonright \qquad\quad \upharpoonleft\downharpoonright \\ & & AgCl \downarrow \quad HNO_3 \end{array}$$

In the mixed solutions, we have **four** ions in quantity, Ag^+ and NO_3^- from the $AgNO_3$, H^+ and Cl^- from the HCl. Before mixing, these were assumed to be in equilibrium with much smaller amounts of undissociated $AgNO_3$ and undissociated HCl respectively. But as soon as we bring all four ions into the same solution, we furnish them with the opportunity of combining with other partners, Ag^+ with Cl^- and H^+ with NO_3^-. AgCl and HNO_3 may also be formed, therefore, in the mixed solutions, each substance in equilibrium with its respective pair of ions. (This is conveniently indicated by the method of writing the equations which is employed above. The student should copy this method in analyzing all double decompositions.)

Now it so happens that one of the new solutes, AgCl, is *practically insoluble in water*. Unless the solutions are excessively dilute, therefore, silver chloride separates out from the solution as a *precipitate*. This precipitation disturbs the existing equilibria by withdrawing practically all silver-ion Ag^+ and chloride-ion Cl^- from the solution, leaving only hydrogen-ion H^+ and nitrate-ion NO_3^- therein in significant quantity.

The reader must note that *any* silver salt added to *any* chloride in solution also gives a precipitate of silver chloride. This can be *predicted* immediately by ionic equations. If, therefore, we learn the properties of a few important positive and negative ions, we learn, at the same time, the properties in solution of *all* the electro-

lytes of which these ions are constituents. This introduces a great simplification into the study of chemistry.

To avoid a common misconception, it must be noted that the electromotive series has no bearing on the tendency of one radical to dislodge another *in double decompositions*. The place of an element in the electromotive series defines its relative activity *when free*, and has to do only with actions where *one free element displaces* (p. 130) *another*. The influences which determine a double decomposition (see p. 226) are such as the insolubility or volatility of a compound, and have little to do with the chemical activity of the compounds concerned and nothing whatever to do with that of the free elements, for these, in fact, are not present at all. Thus, when silver chloride (insoluble) is placed in a solution of potassium iodide KI, it is quickly converted into silver iodide AgI. This happens because silver iodide is still more insoluble than is silver chloride. But free chlorine (the gas) will quickly displace the iodine from silver iodide.

Ions and Conductivity. — Pure water is an exceedingly poor conductor of electricity. The high conducting power of a solution is due essentially, therefore, to the ions furnished by the solute. The actual conductance of any given solution will depend on the *number of ions* between the electrodes, the *number of charges upon each ion* (see p. 304), and the *rate at which the ions move*. The more numerous the ions are, and the more rapidly they migrate towards the oppositely-charged electrodes, the greater will be the number of discharges taking place per second upon each electrode.

The case is like ferrying an army across a river. The number of soldiers passing per hour will depend, (1) upon the number of boats available, (2) upon the speed with which each boat moves, and (3) upon the capacity of each boat. When equivalent instead of equi-molar solutions are compared, the last of these factors, the valence, drops out of consideration.

The rate at which the ions move, under standard conditions, has been carefully determined by methods which are refinements upon the experiments described on pages 311–2. It will suffice at this stage to give a few results. With electrodes one centimeter apart, and with a difference in electrical potential between the positive and negative electrodes of one volt, the velocities in centimeters per hour in very dilute aqueous solution at 18° are as follows: H^+ 10.8, Na^+ 1.26, Ag^+ 1.66, OH^- 5.6, Cl^- 2.12, NO_3^- 1.91. The hydrogen ion is the fastest, the hydroxyl ion holds the second place.

With the help of these figures we can calculate what is the *apparent extent of ionization* of the electrolyte in any solution con-

taining these ions, hydrogen chloride for example. We have already learned (p. 183) that a gram molecular weight of hydrogen chloride contains 6.06×10^{23} molecules. If ionization in solution were complete, therefore, a liter of a normal solution (p. 201) of hydrochloric acid would contain 6.06×10^{23} hydrogen ions, and the same number of chloride ions. These, moving at the rates given above, would give a definite, calculable conductivity. The conductivity actually obtained by experiment with a normal solution of HCl at 18°, however, is only 78 per cent of this calculated value. The conclusion drawn by Arrhenius was that, in normal solution at 18°, hydrochloric acid contains only 78 per cent of free ions, the remaining 22 per cent of solute contributing nothing towards the conductivity. We may express this conclusion by writing the reversible ionic dissociation in the form:

$$(22\%)\ HCl \rightleftarrows H^+ + Cl^-\ (78\%).$$

At other concentrations different degrees of dissociation would be indicated. For example, a 0.5 *N* solution gives 85 per cent of the calculated conductivity, a 0.1 *N* solution 92 per cent, a 0.01 *N* solution 97 per cent. *At very high dilutions, therefore, the ionization becomes practically complete.*

All electrolytes are not, it is quite obvious, ionized to equal extents at the same concentrations. Thus, a normal solution of acetic acid at 18° shows only 0.4 per cent of the calculated conductivity for complete ionization. Even a 0.001 *N* solution is only 12.5 per cent ionized. A fundamental point in the ionic hypothesis of Arrhenius, however, is that ionization always approaches completion as the solution becomes more and more dilute.

It should be clearly noted here by the student that the theory of Arrhenius assumes that, as the concentration of any given electrolyte in the solution is varied, its *extent of ionization changes* while the *mobilities of the ions remain constant.* For most electrolytes, however, on this assumption, the quantitative changes in the degree of ionization with concentration are not at all in agreement with the law of molecular concentration (see next chapter). Many hypotheses have been devised in the attempt to explain this abnormality and, among other explanations, it has frequently been postulated that the rate at which the ions move is *not* independent of concentration, but is a function of the environment in which the ions exist. In other words, it has been suggested that the mobility of an ion must be significantly affected by the forces exerted upon it by other ions in its immediate vicinity, and that the magnitude of such forces must vary considerably with the ionic concentration. We may carry this suggestion to the extreme, of course, by considering the possibility that the *extent of ionization does not change* when the concentration

is changed, and that the *ionic mobilities alone vary.* **This is exactly what is indicated by recent work in the field of strong electrolytes** (see p. 328).

For the present, we shall continue to develop our main argument in terms of the original Arrhenius theory, but the student should remember that, every time the term "extent of ionization" is used, it should be interpreted as "apparent extent of ionization." He should also bear in mind the fact that these "apparent extents of ionization," as derived from conductivity measurements, are of considerable practical importance apart from any question as to the manner of their theoretical interpretation.

Apparent Fractions Ionized in 0.1 *N* Solution at 18°.—The following table shows the approximate degrees of ionization (as obtained from conductivity determinations, for further experimental details, see p. 322) of a number of typical electrolytes in tenth-normal solution in water at 18°. In the case of acids and bases containing more than one displaceable unit of hydrogen or hydroxyl, the kind of ionization on which the figure is based should be particularly noted.

ACIDS

Hydrochloric acid (H^+,Cl^-)	0.92	Hydrofluoric acid (H^+,F^-)	0.085
Nitric acid (H^+,NO_3^-)	0.92	Acetic acid ($H^+,CH_3CO_2^-$)	0.013
Sulphuric acid ($2H^+,SO_4^{=}$)	0.61	Carbonic acid (H^+,HCO_3^-)	0.0017
Oxalic acid ($H^+,HC_2O_4^-$)	0.50	Hydrosulphuric acid (H^+,HS^-)	0.0007
Phosphoric acid ($H^+,H_2PO_4^-$)	0.27	Boric acid ($H^+,H_2BO_3^-$)	0.0001

BASES

Sodium hydroxide (Na^+,OH^-)	0.91	Barium hydroxide ($Ba^{++},2OH^-$)	0.77
Potassium hydroxide (K^+,OH^-)	0.91	Ammonium hydroxide (NH_4^+,OH^-)	0.013

SALTS

Potassium chloride (K^+,Cl^-)	0.86	Sodium bicarbonate (Na^+,HCO_3^-)	0.78
Sodium chloride (Na^+,Cl^-)	0.84	Barium chloride ($Ba^{++},2Cl^-$)	0.76
Potassium fluoride (K^+,F^-)	0.85	Silver sulphate ($2Ag^+,SO_4^{=}$)	0.70
Sodium nitrate (Na^+,NO_3^-)	0.83	Zinc sulphate ($Zn^{++},SO_4^{=}$)	0.40
Potassium nitrate (K^+,NO_3^-)	0.83	Copper sulphate ($Cu^{++},SO_4^{=}$)	0.40
Silver nitrate (Ag^+,NO_3^-)	0.81	Mercuric chloride ($Hg^{++},2Cl^-$)	<0.01
Sodium acetate ($Na^+,CH_3CO_2^-$)	0.79		

Ionization and Chemical Activity.—From a consideration of the above figures and the results given by other acids, bases and salts, the following important conclusions may be drawn:

1. **Salts,** with the exception of a few mercuric salts, are all *extensively ionized* in 0.1 *N* aqueous solution. The salts which dissociate into univalent ions show the greatest apparent degree of ionization. Compare, for example, the series sodium chloride, silver sulphate, copper sulphate.

2. **Acids** show the most extreme differences in their degrees of ionization. That is to say, equivalent solutions contain very different concentrations of hydrogen-ion. Since their *activity* as acids depends upon this substance (p. 313), it follows that acids will exhibit very marked differences in chemical activity (for example, in their action on metals). In fact, they may be divided roughly into three classes:

(*a*) *Strong acids,* such as hydrochloric acid, nitric acid, sulphuric acid. These substances are highly ionized in 0.1 *N* solution. Their solutions conduct the electric current excellently, and are chemically most active.

(*b*) *Transition acids,* such as phosphoric acid, hydrofluoric acid. These substances are significantly, but not highly, ionized in 0.1 *N* solution. Their solutions conduct fairly well, and show moderate activity.

(*c*) *Weak acids,* such as acetic acid, carbonic acid, boric acid. These substances are scarcely ionized at all in 0.1 *N* solution. Their solutions conduct the current very poorly, and exhibit little activity as acids.

That a difference in the activity of different acids does exist may be shown, roughly, by placing similar pieces of the same metal, say zinc, in equal volumes of various normal solutions of acids, such as hydrochloric, sulphuric, and acetic. The hydrogen is evolved more rapidly by the first than by the second, and very much faster by either than by the last. Naturally, the first is sooner exhausted, while the third acts in its slow way for a very long time before being all used up. In the third case few ions of hydrogen are at hand at any one moment, but more are formed continuously from the molecules, to take the place of those displaced. Thus the total amount of hydrogen obtained from each acid is finally the same. It is *the speed of evolution alone which is different* and shows the differing concentrations of the hydrogen-ion.

3. **Bases** also show very extreme differences in their degrees of ionization. We have two main classes — *strong bases,* such as sodium hydroxide, barium hydroxide; and *weak bases,* such as ammonium hydroxide. Between these fall certain *transition bases,* such as silver hydroxide (which is only very slightly soluble, but which is noticeably stronger than ammonium hydroxide) and some organic derivatives of ammonium hydroxide.

4. **Water** itself is both an exceedingly weak acid and an exceedingly weak base. It breaks up into the two ions H^+ and OH^- to a very minute extent indeed. At the ordinary temperature the fraction ionized is less than 0.000,000,002. Pure water consequently conducts the electric current practically not at all. The ionization

of water, however, is a factor of vital importance in the explanation of certain reactions, as we shall see later.

Ions and Vapor-Pressure, Boiling-Point and Freezing-Point Abnormalities. — The cause of the abnormal changes in these three physical properties, exhibited by solutions of electrolytes, will now be evident. According to the theory of Arrhenius, a solution of sodium chloride containing one gram-molecular weight of salt in 1000 g. of water gives almost *twice the calculated effect* in each case, because almost all of the solute is present as Na^+ and Cl^-, instead of as undissociated NaCl. The number of solute molecules present is almost *doubled* by ionization. Similarly a dilute solution of ferric chloride shows nearly *four times* the normal change in freezing-point lowering, for example, owing to the fact that the majority of $FeCl_3$ molecules, as indicated by conductivity data, are broken up into *four* ions, Fe^{+++} and $3Cl^-$.

Solutions of weak electrolytes, such as acetic acid and ammonium hydroxide, exhibit practically normal results, because only an insignificant fraction of the solute is broken up into ions.

Careful measurements show a close agreement in apparent extents of ionization, as determined by the two independent methods, conductivity ratio and freezing-point depression, throughout the whole list of hundreds of electrolytes. The agreement in general is so good that it used to be considered, indeed, as one of the strongest confirmations of the validity of the Arrhenius ionization hypothesis. Minor discrepancies were known to exist, it is true, particularly in more concentrated solutions, but it was assumed that specific effects (such as interaction with the solvent water, or *hydration*) sufficed as an explanation. Nevertheless, it has more recently been recognized that not only are the small divergences between the two methods, when all precautions are taken to insure accurate results, considerably in excess of any possible experimental error, but also that theoretical considerations necessitate slightly different values for the conductivity ratio and the freezing-point abnormality for *any* solution of a strong electrolyte of finite concentration. The more intimate investigation of these differences has been of considerable service, in fact, in the development of a logical modification of the Arrhenius theory (see p. 328) to cover the behavior of *strong electrolytes*. For practical purposes, however, the two methods may be regarded as in substantial agreement.

Exercises. — 1. Which are the anions and which the cations in the substances whose formulæ are given on p. 291?

2. Using the models given on p. 304, make the ionic equations representing the ionization of all the acids, bases, and salts, the formulæ of which are given on p. 292.

3. Make an ionic equation (p. 313) for the displacement: (*a*) of hydrogen from dilute hydrochloric acid by magnesium; and (*b*) of silver from silver nitrate solution by zinc.

4. Is it correct to say that the action which takes place when zinc is put

into a solution of copper sulphate solution consists of a transfer of positive charges from copper ions to atomic zinc, induced by the greater affinity of zinc for positive electricity? Re-word the statement in terms of electrons (p. 313)

5. Rewrite the double decompositions on p. 292 in full ionic form.

6. Why does a solution of 0.1 *N* hydrochloric acid conduct the current nearly twice as well as a solution of 0.1 *N* sodium hydroxide, and nearly four times as well as a solution of 0.1 *N* sodium chloride?

7. From the results given on p. 295, calculate the apparent degree of ionization of sodium chloride in a solution containing 1 gr. mol. wt. NaCl to 1000 g. water (*a*) at the boiling-point, and (*b*) at the freezing-point.

8. From the results given on p. 296, calculate the apparent degree of ionization of potassium chloride in a solution containing 1 gr. mol. wt. KCl to 1000 g. water at 20°.

9. With solutions of the following substances, state, (*a*) what will be the products of electrolysis, (*b*) whether each is primary or secondary, and (*c*) how they may be isolated in each case: Potassium chlorate, potassium iodide, potassium iodate, silver sulphate, sodium peroxide, sodium fluoride.

10. How many coulombs are carried by or will deposit: 20 g. of silver, 15 g. of antimony, 30 g. of chlorine, 60 g. phosphate-ion (PO_4)?

11. What current strength (in amperes) is required to deposit: 20 g. of silver in an hour, 100 g. of iodine in 5 minutes, 60 g. of antimony in 3 hours?

12. 25 g. of sodium nitrate are dissolved in 1000 g. of water. The degree of ionization of the salt in the solution is 70 per cent. What is the freezing-point of the solution?

13. 20 g. of barium chloride are dissolved in 1000 g. of water. The degree of ionization is 77 per cent. What is the freezing-point of the solution? [Remember that for every 100 molecules of $BaCl_2$ added you have 23 $BaCl_2$ undissociated, 77 Ba^{++}, and 154 Cl^-.]

14. 10 g. of sodium sulphate are dissolved in 600 g. of water. The boiling-point of the solution at 760 mm. is 100.15°. What is the degree of ionization?

15. At 20° 100 g. of water dissolve 204 g. of sugar $C_{12}H_{22}O_{11}$ and only 74 g. of calcium chloride. Nevertheless calcium chloride is a much more deliquescent substance than sugar. Explain the apparent discrepancy. [*Note:* There are three distinct reasons which you should be able to advance.]

16. A current is passed simultaneously through five cells connected up in series, containing, respectively, solutions of the following substances: sulphuric acid, silver nitrate, cupric sulphate, gold chloride $AuCl_3$ and stannic chloride $SnCl_4$. After the electrolysis has proceeded for a sufficient length of time, the amounts of the different elements separated at the cathodes are determined. The results are as follows: Hydrogen 0.084 g.; Silver 8.99 g.; Copper 2.65 g.; Gold 5.48 g.; Tin 2.47 g. Calculate the *equivalent weights* of Ag, Cu, Au and Sn on the basis Oxygen = 8. What is the valence of the positive ion in each solution?

17. Plot the freezing-point depression curves for dilute aqueous solutions of sodium chloride, calcium chloride and ferric chloride from the following data:

G. mols. NaCl in 1000 g. water	0.02066	0.04122	0.08354
Freezing-point depression, ° C.	0.07357	0.1453	0.2897
G. mols. $CaCl_2$ in 1000 g. water	0.0100	0.0503	0.1006
Freezing-point depression, ° C.	0.0513	0.2437	0.4823
G. mols. $FeCl_3$ in 1000 g. water	0.0210	0.0369	0.0843
Freezing-point depression, ° C.	0.145	0.245	0.508

18. Turn back now to Exercise 37, Chapter XII, and plot the data for mannite on the same diagram, converting the values given into g. mols. in 1000 g. water. Compare your four curves, and make the following tests upon them:

(*a*) Do they start out from 0° with initial slopes in the ratios 2 : 3 : 4 : 1? Why?
(*b*) Do the first three curves exhibit gradually decreasing slopes with increasing concentration of salt, while the slope of the fourth curve remains constant? Why?
(*c*) Does the slope of the third curve decrease more rapidly than that of the second, and the slope of the second more rapidly than that of the first? Why (two reasons)?
(*d*) Calculate, from the curves, the percentage dissociation of each salt at a concentration of 0.05 weight-molar.

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CHAPTER XIX

IONIC EQUILIBRIA AND THE THEORY OF COMPLETE IONIZATION

Now that we have presented the main features of the ionization theory of Arrhenius, we shall proceed to amplify the argument at certain points, in order to impress upon the student the primary importance of this theory and to accustom him to its use and its limitations in chemistry by the consideration of some additional experimental illustrations. Simultaneously, the ground now having been sufficiently prepared, certain aspects of the modern theory of complete ionization of strong electrolytes will be discussed in some detail.

Determination of Apparent Degrees of Ionization. — Ordinarily, it is the *resistance* which a solution presents to the passage of the electric current that is actually measured. The unit of electrical resistance is the **ohm,** which is related to the ampere and the volt by the definition that one ampere is the current produced in a conducting medium with a resistance of one ohm and with a potential difference between the electrodes of one volt (see also p. 838). For our present purposes, however, we are not so much interested in the resistance of any particular solution as in its conductivity, which, being the reciprocal of the resistance, is expressed in **reciprocal ohms.** The **specific conductivity** (κ) of a solution is the value so obtained when one cubic centimeter of the solution is introduced into a cell with electrodes one square centimeter in size and one centimeter apart. But in order that our results may have fundamental chemical significance, we must reduce the figures for solutions of different concentration to standard conditions by calculating what the conductivity of each would be if the electrodes extended into space so that, between them, there was always one gram-equivalent of the electrolyte. This we call the **equivalent conductivity,** Λ. If the concentration of the solute is such that we have one gram-equivalent present in v liters of the solution (in other

words, if the normality of the solution is $1/v$) then the equivalent conductivity at this dilution (Λ_v) is given by the simple relation: $\Lambda_v = 1000\,\kappa v$.

The following numbers show the equivalent conductivities at 18° of solutions of four different substances, expressed in reciprocal ohms. It will be seen from inspection of these figures that, for the first three substances, the equivalent conductivity does not increase much when a solution containing one equivalent in a liter is diluted ten times, and that further dilutions, no matter how extensive, produce a still smaller effect. The case of acetic acid requires separate consideration (see next section).

Equivalent Conductivity (Λ)	$v = 1$	$v = 10$	$v = 100$	$v = 1000$	$v = \infty$ (Calc.)
Hydrochloric acid	301.0	351.0	370.0	379.0	384
Sodium chloride	74.4	92.5	103.0	107.8	110
Sodium acetate	41.2	61.1	70.2	75.2	78
Acetic acid	1.32	4.6	14.3	41.0	(352)

The approach to a maximum of conductivity reached in these first three cases, at $v = 1000$, indicates that practically the whole of the material has, by then, assumed the ionic form. Theoretically the absolute maximum would be reached at infinite dilution. The conductivity of one gram-equivalent of substance in more limited dilution is assumed, according to the theory of Arrhenius, to indicate the proportion of ions existent at this dilution, any molecules, still present, being without influence on conductivity. Thus the ratio of the conductivity at a given dilution to the maximum conductivity is equal to the proportion of the whole material ionized at the given dilution. From a series of measurements for any particular substance at different dilutions, after the results have been plotted, we can usually ascertain the limiting, maximum conductivity by graphic extrapolation (see last column in above table). The best method to use is that of Kohlrausch, in which Λ is plotted against the square root of the concentration c (the reciprocal of v), since this gives for most electrolytes practically a straight line, which can readily be extended to $c = 0$. If Λ_v is the conductivity of an equivalent of the substance dissolved in v liters of water, and Λ_∞ the conductivity extrapolated to infinite dilution, then Λ_v/Λ_∞ is the proportion of molecules apparently ionized in the former solution.

A glass trough and ammeter* (Fig. 111) may be used to illustrate this principle. The electrodes are long strips of copper foil, which pass down to the foot of the trough. After placing the two instruments in circuit with a source of electricity, we first pour very pure water into the cell. With this arrangement, the ammeter does not indicate the passage of any measurable current of electricity. A small quantity of concentrated (36 per cent) hydrochloric acid is next cautiously added through a long-stemmed dropping funnel, so that it forms a shallow layer below the water, and the funnel is withdrawn. The situation at this stage is that a definite amount of hydrogen chloride dissolved in a *small* amount of water fills what was before practically a non-conducting gap in the electric circuit. The deflection of the needle in the ammeter indicates that a feeble current is now able to pass through the circuit. When, however, we stir the surface of the acid very gently with a thin glass rod, the ammeter instantly responds, showing a large increase in conductivity. As we stir, the conductivity increases, and the increase

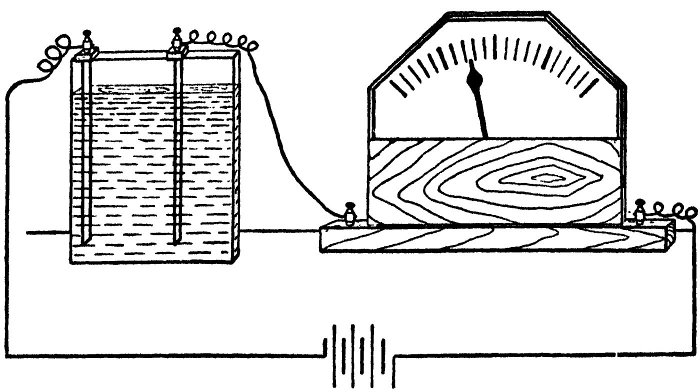


FIG. 111. Apparatus to illustrate Conductivity Changes.

ceases only when the liquid has become homogeneous. Introduction of an additional supply of water will improve the conductivity still more, but the effect becomes less and less, until no change on further dilution is perceptible. The *amount* of hydrochloric acid between the electrodes has not altered during the experiment, yet the conducting power has vastly improved. If we could conveniently have started with only liquefied, dry hydrogen chloride in the cell, we should have observed the whole range of changes from zero to the maximum.

The Case of a Little-Ionized Substance. — Acetic acid, a feebly ionized substance, as the table shows, conducts very poorly in concentrated solution and, while the equivalent conductivity improves

* An ammeter (ampere-meter, see p. 305) is an instrument by means of which the number of coulombs of electricity passing through the solution per second is indicated. In the above experiment, an ammeter of low resistance must be used.

with dilution, it is not possible experimentally to observe any approach to the maximum value. The equivalent conductivity, in cases like this, is still far removed from the maximum at dilutions at which, with other substances, the maximum is nearly attained.

In cases like acetic acid, the equivalent conductivity at infinite dilution cannot be estimated by extrapolation. But fortunately another method is available. The values 384, 110, and 78 for Λ_∞ in the cases of the first three substances in the table on p. 323 can be reached by extrapolation, and represent the conducting powers of equal numbers of ions, for there are equal numbers of equivalents present and no molecules remain unionized. These values are unequal solely because of the differing speeds of the ions concerned. Each of them derives its value from numbers representing the relative speeds of the two ions present, and must be the sum of these two numbers. If, therefore, we measure the relative speeds of the two ions (p. 315) of one of the substances, we can divide the value of Λ_∞ in this proportion and learn the part which each ion contributes to the total. Dividing 384 in this way we get the speed of $H^+ = 318$ and of $Cl^- = 65.9$. Dividing Λ_∞ for sodium acetate (78), similarly, we get the speeds $Na^+ = 44.4$ and $CO_2CH_3^- = 33.7$. The speeds of Cl^- and Na^+ together $(65.9 + 44.4 = 110.3)$ must then equal Λ_∞ for NaCl and, as we see, they do. Similarly, the speeds of H^+ and $CO_2CH_3^-$ together $(318 + 33.7 = 351.7)$ must equal Λ_∞ for HCO_2CH_3, although we cannot observe the latter directly. This method can be applied to all of the less highly ionized acids and bases, for their sodium and potassium salts belong invariably to the class of substances which are highly ionized, and for which, therefore, Λ_∞ can be determined accurately by extrapolation.

Influence of Temperature on Ionization. — With most strong electrolytes, the conductivity ratio Λ_v/Λ_∞ for a fixed dilution decreases very slowly as the temperature is raised. With weak electrolytes, the fraction ionized frequently increases to a maximum and then decreases with further rise of temperature. The weaker the electrolyte, the higher the optimum temperature for ionization, as a general rule. Thus ammonium hydroxide and acetic acid exhibit maxima of ionization around ordinary room temperatures, while water gives rapidly increasing values over the whole range between 0° and 100°, and only by heating in a closed cell under considerable pressure can the maximum ionization be established at about 250°. Above this temperature, the ionization of water begins to diminish once more. In all such cases, the heat of ionization changes its sign, being at first negative, and, beyond the maximum, positive (compare pp. 284, 333).

Ionic Equilibrium. — From the fact that the proportion of molecules ionized is apparently found by conductivity measurements to

become greater as more and more of the solvent is added (p. 323), and that removal of the solvent diminishes the proportion of ions to molecules, and finally leaves the substance entirely restored to the molecular condition, the theory of Arrhenius assumes that ionization (compare pp. 299, 303) is a reversible action and therefore a true dissociation. The molecules and their ions adjust themselves like the components in any case of chemical equilibrium (pp. 268–70):

$$RX \rightleftharpoons R^+ + X^-.$$

This equation is, formally, of precisely the same nature as that for phosphorus pentachloride vapor (pp. 272–8), and the discussion of the latter should be reëxamined and applied by the reader. The sole difference is that here change in volume is effected, not by compression or by release of pressure, but by removing or adding water. **The adjustment to a condition of equilibrium,** however, **seems to be instantaneous where ions are concerned,** while in other chemical actions it always takes a perceptible, and often a considerable interval of time.

The mode of formulation previously used (p. 272) may be employed here. If [RX], [R^+], and [X^-] stand for the molecular concentrations (numbers of moles per liter) at equilibrium of the molecules, and the two ions, respectively, we have an equilibrium constant (compare p. 273), in this case called the **ionization constant:**

$$\frac{[R^+] \cdot [X^-]}{[RX]} = K.$$

If x is the degree of ionization when one gram molecular weight of solute is dissolved in v liters of solution, then we have the expression (compare p. 277): $x^2/(1-x)v = K$.

The Case of Weak Electrolytes. — For the application of the principles outlined above, the behavior of acetic acid, a slightly ionized acid, will serve as an illustration. When acetic acid is dissolved in water, it is ionized thus:

$$CH_3.COOH \rightleftharpoons H^+ + CH_3.COO^-.$$

According to the law of molecular concentration (p. 273):

$$\frac{[H^+] \cdot [CH_3.COO^-]}{[CH_3.COOH]} = K,$$

and the numerical value of K should remain unchanged whatever the concentration of the solution may be.

A numerical example will show that this law (first applied to weak electrolytes by Ostwald, and hence known as **Ostwald's dilution law**) expresses the facts with considerable exactness. The data in regard to acetic acid at 25° are as follows (compare p. 316):

Acetic Acid. 25° C.

Concentration (in normalities)	*Percentage Ionized*	$K \times 10^5$
0.125	1.193	1.80
0.0625	1.673	1.79
0.03125	2.380	1.82
0.01562	3.33	1.79
0.00781	4.68	1.79
0.00391	6.56	1.80
0.00196	9.14	1.80
0.00098	12.66	1.78

In other words, although the last solution is more than a hundred times more dilute than the first, and the degree of ionization has increased more than ten times, the **ionization constant** remains close to the value 1.80×10^{-5} and is essentially constant within the limits of experimental error.

The Case of Strong Electrolytes. — When conductivity data, like the above, are analyzed in the same way for more highly ionized substances, the values obtained for K at different concentrations are *not* constant. It is recognized that with this class of substances the measurements of degrees of ionization by the conductivity method are inaccurate, and the cause of the discrepancy may now be briefly discussed.

In a preceding chapter (p. 278), we have already called attention to the fact that the law of molecular concentration is merely a limiting case, and that it cannot possibly apply in its simple form to any system in which the attractive forces between the various reacting molecular species are appreciable. Now in solutions of strong electrolyes, where the concentrations of positively and negatively charged ions are large, the proximity of the ions to one another in the solution will necessarily be such that the electrical forces imposed upon any one ion by its neighbors must exercise a considerable effect upon it. In other words, its environment will not be the inert environment postulated by strict kinetic-molecular theory for the applicability of the law of mass action, and the

apparent concentration or activity of the ions will, consequently, by no means be identical with their true concentration in the solution. Only in solutions of weak electrolytes, where (in view of the much smaller ionic concentrations) the inter-ionic forces are of much smaller magnitude, can the equation as derived above be expected to apply, and here indeed it is found by experimental test to apply with great precision. For weak electrolytes, therefore, the Arrhenius theory is practically in accordance with the experimental facts. To explain the abnormality of strong electrolytes, however, we need to modify the theory very considerably.

Complete Ionization. — Professor A. A. Noyes, as long ago as 1908, referred to the possibility that the so-called undissociated fraction of a salt in solution, say NaCl, might exist in a *potentially ionized* condition $[Na^+Cl^-]$, the atoms being oppositely charged but held together by their mutual attraction (*bound ions*, see p. 298). The work of the Braggs on crystal structure indicated subsequently that *no* molecules of NaCl are present in the solid salt, the crystal structure consisting of alternate sodium and chlorine ions arranged in a cubic lattice (see p. 68). The obvious extension of this idea to solutions was somewhat delayed, but in 1923 a logical presentation of the **theory of complete ionization** was put forward by Debye and Hückel. The work of these investigators is complicated by the very thoroughness of their mathematical treatment, yet their argument is based upon the two simple assumptions that, in dilute aqueous solution, strong electrolytes are *completely dissociated* and that any departures from the law of ideal solutes are due entirely to *electrical forces between the ions*. The "activity" of any single ion is dependent upon the density of its "ionic atmosphere," and the variation in this activity with total ionic concentration may be readily calculated.

If several simplifying assumptions are made, the theory of Debye and Hückel leads for dilute solutions of strong electrolytes to a law previously discovered empirically by Kohlrausch, which may be stated as follows: For any given electrolyte at a series of different concentrations, the *apparent fraction un-ionized* (as derived from conductivity determinations, see p. 323) varies as the square root of the concentration.

Actually, of course, the lower conductivity ratios obtained at higher concentrations are *not* due to any significant decrease in the degree of ionization of the electrolyte, but to a decrease in the mobility of the ions (see p. 316). The undissociated molecule of the Arrhenius theory, for strong electrolytes,

does not have any real existence, but the conception may readily be modified so as to represent the extent to which the forces imposed upon an ion by its neighbors restrict its freedom.

If we set our attention on any single ion, say a positive ion R^+, in a solution of an electrolyte RX, we must recognize the fact that it will exercise attractive forces on every negative ion X^-, and repulsive forces on every other positive ion R^+, in its vicinity. This involves the consequence that a small sphere surrounding our ion will contain more negative ions X^- than positive ions R^+. In other words, our positive ion is situated in a negatively-charged environment, and the same is true of all other positive ions in the solution, while all negative ions will be surrounded by a positively-charged envelope. When a current is passed through the solution, therefore, attracting our positive ion towards the cathode, its surrounding "atmosphere" experiences an opposite attraction towards the anode, and the result is similar to that of a brake on the motion of the central ion — its mobility is lowered.

The more concentrated the solution, the smaller will be the average distance between the ions and the greater the intensity of the oppositely-charged envelope around each ion in the solution. Consequently, the "drag" on the motion of the ions varies with the concentration, and exact mathematical analysis shows that, in very dilute solutions, it should vary *as the square root of the concentration.* The experimental results are found to be in satisfactory concordance with this (see p. 323).

One other point is worth noting in this connection. A bivalent ion must obviously exercise more powerful attractive and repulsive forces on its neighbors than a univalent ion, and at equivalent concentrations will therefore experience a stronger "drag." The *apparent extents of ionization* (as deduced by conductivity measurements) for a series of salts at any fixed concentration ought then to be greatest for salts with two univalent ions, falling off progressively for salts of more complex types. This is exactly what we find experimentally, as will be seen from the table on p. 317.

Double Decomposition. — Returning now to our example of silver nitrate and hydrochloric acid (p. 314), it is instructive to see in what guise the reaction appears when complete ionization is postulated. We obtain, as follows, the equation:

$$[Ag^+ + NO_3^-] + [H^+ + Cl^-] \rightarrow AgCl\downarrow + [H^+ + NO_3^-].$$

Canceling out the common factors on both sides of the equation, we find that *the only interaction taking place is the production of the insoluble body:*

$$Ag^+ + Cl^- \rightarrow AgCl\downarrow.$$

The sole change that has befallen the ions of nitric acid is that they have been transferred from two separate vessels into one.

A still more striking example is the interaction of silver sulphate and barium chloride in solution:

$$[2Ag^+ + SO_4^{=}] + [Ba^{++} + 2Cl^-] \rightarrow 2AgCl\downarrow + BaSO_4\downarrow.$$

Here we are left at last, if we use equal volumes of equivalent solutions, with a mixed precipitate of silver chloride and barium sulphate, and a solution which is practically pure water.

This experiment may be carried out in the apparatus shown in Fig. 111 (p. 324). The silver sulphate solution is first introduced into the cell, and an equivalent quantity of barium chloride solution, weighted with sugar to increase its density and prevent mixing, is carefully run in beneath it by means of a funnel. (It is preferable to separate the two solutions altogether by running a little pure sugar solution through the funnel before adding the barium chloride.) When the current is turned on, the ammeter indicates that the two solutions, before mixing, possess considerable conductivity. After the solutions are thoroughly mixed by stirring, the pointer drops back practically to zero.

The foregoing formulation and explanation apply to every case of mixing solutions of electrolytes where precipitation occurs, that is, where the products are insoluble acids, bases, or salts. That precipitation, however, is *never absolutely complete* is an important point, the consequences of which will be examined in detail in a later chapter (pp. 754–61).

If the least soluble of the four salts concerned in a double decomposition is still fairly soluble, more concentrated solutions are required to secure even very incomplete precipitation. The interaction of hydrogen chloride and sodium-hydrogen sulphate (p. 225) is of this nature.

In spite of the fact that most double decomposition reactions may, as in the case of $Ag^+ + Cl^- \rightarrow AgCl$, be condensed into a simpler combination reaction, it does not seem justifiable (as some enthusiasts would hold) to abandon this type of chemical change entirely and regard it as a mere misconception. Most examples of the three other varieties of chemical change may also be modified, by analysis, into a single class — oxidation-reduction reactions (see p. 840) — but it is none the less convenient to retain them as distinct types in ordinary chemical work. From a practical point of view, the student who mixes solutions of silver nitrate and sodium chloride in the laboratory should not be allowed to forget the fact that, besides the one obvious product of the reaction (a precipitate of silver chloride), there must also *always* be a second product (here a solution of sodium nitrate). In many instances (see for example pp. 367, 385, 438) this second product is undoubtedly the more important of the two.

A good illustration of the advisability of utilizing double decomposition equations in the teaching of chemistry is afforded by the very first example encountered in this volume — the action between salt and sulphuric acid (p. 225). Could the condensed equation $H^+ + Cl^- \rightarrow HCl$ possibly give the student a satisfactory insight into the mechanism of this reaction?

Application in Chemical Analysis. — Since the larger number of ordinary chemical substances are electrolytes, and the most rapid and simplest chemical changes take place when they are in

solution, the various reactions of their solutions are employed as tests for the substances in question. An advantage of the use of the solutions is that they contain a mixture of two independent materials, the anion and the cation, and when these have been identified successfully the salt from which they were formed is known. The simplicity to which chemical analysis is thus reduced may be seen when we consider that twenty-five common metals with twenty-five negative radicals might give a total of over six hundred different salts. If the distinct properties of *each* of these had to be considered, the identification of an unknown substance would be very difficult. In solution, however, the problem becomes much easier. A solution made from a single salt will, in general, contain but two substances (see, however, p. 291), and the problem thus reduces itself to ascertaining which two, out of a total of fifty, are present in any particular case. This is easier than investigating six hundred possibilities.

As as example of the method, let us suppose that we look first for the positive ion. Most systems of analysis begin by the addition of a solution containing chloride-ion, generally dilute hydrochloric acid, to the liquid. If an ion is present which in combination with chloride-ion gives an insoluble compound, a precipitate will appear. Amongst the common positive ions but three are of this kind, namely, silver-ion, mercurous-ion, and lead-ion. So that the precipitate, if it appears, is a chloride of one of these three metals, and the matter of distinguishing between the three is quickly disposed of by further examination of its properties. If no precipitate comes out, then these three metals are probably absent, and some fresh ion capable of precipitating another set of positive ions is introduced (see Chap. LIII). Thus by a process of elimination we quickly find out whether any metal ion is present, and, if so, precisely which one it is.

The language of analysis is frequently somewhat loose. Thus we speak of the addition of a silver salt to a solution as being a "test for chlorine." As a matter of fact, it is not a test for chlorine. It is not intended as a test for free chlorine, nor will it show the presence of chlorine in many states of combination. It is simply a test for ionic chlorine Cl^-, and cannot give us information in regard to the presence or absence of any other form of the element. So the wet-way tests for "copper," "silver," etc., so called, are tests for the ionic forms of these elements, and not for the presence of the element in every form. Even the two kinds of copper and mercury ions, Cu^{++}, Cu^+, Hg^{++}, Hg^+, must be classed as distinct substances. Thus, the last is precipitated by chloride-ion while the second last is not, mercuric chloride $HgCl_2$ being soluble.

Thermo-neutrality. — When dilute solutions of salts containing no common ion are mixed, and no precipitation occurs, **no thermal effect** is observable (except in special cases, see *complex ions* below). This fact has been known since 1842 as the **law of thermoneutrality.** We conclude, then, that when completely ionized substances are mixed, **and the possible products are also completely ionized, soluble substances,** then **practically no chemical action occurs.** This rule applies to dilute solutions of almost all soluble salts (p. 317) and to mixtures of salts with the strong acids or bases.

Conversely, when two electrolytes are mixed, **an extensive chemical change does ensue in four cases,** namely:

1. When one of the possible products is an insoluble substance and **precipitation** occurs, for this removes the ions used to form the insoluble body.

2. When one of the possible products is **volatile** and its liberation as a gas removes the ions forming it from the solution (see p. 225).

3. When one of the possible products, although soluble, is **little ionized,** for this likewise removes the ions required to form molecules of the product. We shall proceed to discuss this third important class of actions in the next section.

4. When interaction between the simple ions present in the original solutions produces stable **complex ions.** Discussion of this point must be deferred until later chapters (pp. 686, 788).

Neutralization. — We may now consider the case of **mixing dilute** (say decinormal) **solutions of two electrolytes** where one is **an acid** HX and one **a base** ROH. According to the theory of Arrhenius, we obtain the double decomposition:

$$\begin{array}{rcl} HX & \rightleftarrows & X^- + H^+ \\ ROH & \rightleftarrows & R^+ + OH^- \\ & & \quad\updownarrows \qquad \updownarrows \\ & & \quad RX \qquad H_2O \end{array}$$

The general plan of all interactions of acids and bases is shown in this formulation. When both acid and base are typical strong electrolytes, as in the case of HCl and NaOH, then the substances in the solutions before mixing are entirely ionic. After mixing, however, the crosswise union, $H^+ + OH^- \rightleftarrows H_2O$, is all but complete, for water is hardly ionized at all (p. 318). Practically all the

H^+ and OH^- combine, then, to form water, which thenceforth is simply a part of the solvent. The Cl^- and Na^+, however, remain as free ions in the solution, and strictly speaking no sodium chloride is formed until the solution is evaporated. The same will apply (changing the names of the ions of the salt) whenever any highly ionized acid and base come together. Thus we may write **one simple equation for all neutralizations of strong acids and bases:**

$$H^+ + OH^- \rightarrow H_2O,$$

without omitting anything essential.

Confirmations of This View of Neutralization. — That these inferences are correct is shown by many facts. The most conspicuous of these is the fact that, when *equivalent* amounts (p. 201) of *strong* acids and bases are used, the mixture is *without action* either *on red or on blue litmus*. It is **neutral** to indicators (p. 337) — hence the term **neutralization** is applied to the operation of mixing an acid and a base. Specifically, the absence of effect upon litmus demonstrates the practical absence of hydrogen-ion H^+ and of hydroxyl-ion OH^-, alike, in the product, and confirms the theory.

Again, a considerable thermal effect accompanies neutralization. But, in the cases we are discussing, that is where *strong* bases and acids are employed, the heat liberated by use of gram equivalent weights at 18° is *always the same*, namely 13,700 calories. That it is always the same confirms our theory, for practically the whole change is always the formation of 18.016 g. of water from the ions. The thermochemical equation at 18° thus reads:

$$H^+ + OH^- \rightarrow H_2O + 13{,}700 \text{ cal.}$$

Still again, when we place the acid and base in the cell (Fig. **111**, p. 324, so that the one forms a layer beneath the other, and watch the ammeter while we mix the solutions, a marked *decrease* in the current passing through the cell is noticed. This also confirms our theory, for it is our belief that one-half of the ions, namely the H^+ and OH^-, disappear as such during the action. The decrease is, in fact, to much less than half the reading before mixing, because the two speediest ions have been removed.

When less highly ionized acids or bases are used, the only difference is that there are significant amounts of the molecular materials present, before the solutions are mixed. But the removal of the H^+

and OH^- ions permits the molecules of the acid and base to dissociate, so that the final products are water and the ions of a salt, as before.* When either the acid or the base employed is *very weak,* however, the tendency of water to break up into H^+ and OH^- must be taken into consideration (see **hydrolysis,** p. 408).

The foregoing formulation and explanation apply to every case of mixing solutions of electrolytes, where a very slightly ionized substance is one of the products, that is, when water, or a feeble acid (p. 367), or a feeble base (p. 511) is formed. We may note that this is a **third method** (compare p. 282) **of driving a reversible reaction practically to completion,** which is very frequently utilized by chemists in carrying out reactions.

When we employ very concentrated solutions, or use less completely ionized, or insoluble acids and bases for neutralization, the heats of neutralization are not alike, but different in every case. Thus, for dilute solutions of sodium hydroxide and hypochlorous acid, the latter a slightly ionized, soluble acid with the formula HOCl, the thermochemical equation is as follows:

$$NaOH + HOCl \rightarrow H_2O + NaOCl + 9{,}840 \text{ cal.}$$

Since the sodium hypochlorite is fully ionized, the only difference between this case and the preceding one is that the hypochlorous acid is largely in the *molecular* condition to start with, and that here, in addition to the union of hydrogen and hydroxyl ions, we have a continuous dissociation of the hypochlorous acid accompanying the neutralization. The fact that here the heat produced is much less than before, shows that the dissociation of this acid is associated with the *absorption* of heat.

Similarly with bases, we find that the neutralization of ammonium hydroxide, a feebly ionized base, with any active acid, gives a heat of neutralization below the normal:

$$NH_4OH + HCl \rightarrow H_2O + NH_4Cl + 12{,}200 \text{ cal.}$$

Here again the salt produced is fully ionized. Thus the ionization of the ammonium hydroxide (see, however, p. 514) must have consumed an appreciable part of the heat of neutralization, which would otherwise have reached the normal figure of 13,700 calories.

Volume Change in Neutralization.—When the volumes of the solutions of *active* acids and alkalies are carefully measured before being mixed, and compared with the volume of the neutral mixture, an expansion is always

* Thus, with acetic acid and ammonium hydroxide, water and ammonium acetate are formed. If this neutralization is carried out in the cell shown in Fig. 111, the conductivity before mixing is very slight. After mixing, the number of ions is greatly increased, and the conductivity also increases markedly.

found to have occurred. When one liter of a normal solution of each substance is taken at starting, the volume of the mixture is always 20 c.c. greater than that of the component liquids. This is rather remarkable, because the chemical change has produced only 18 c.c. of water, yet the volume of the water appears to be 20 c.c. *greater* than that of the ions from which it was formed. This shows that the change involves more than the mere union of the ions. The electric charges on the ions cause a high internal pressure, called **electrostriction,** especially in the molecules of water immediately sur-

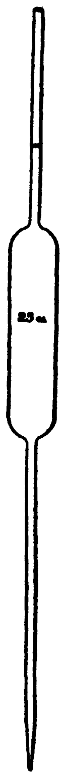


FIG. 112. Pipette.

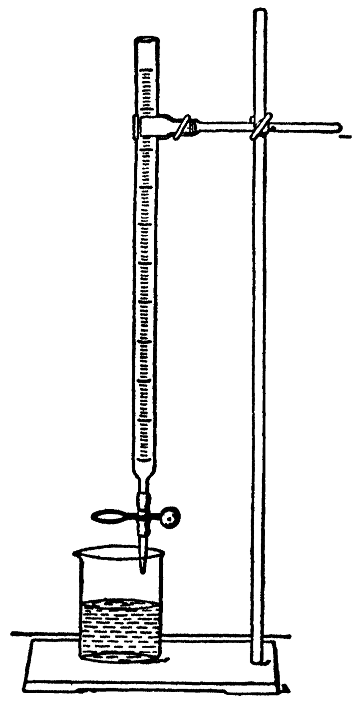


FIG. 113. Burette.

rounding each ion, and the liquid is compressed. When the ions unite, the pressure is reduced, and expansion occurs. When less highly ionized acids and bases are used, the alteration in volume is irregular, since it is affected by the occurrence of other changes than the mere union of hydrogen-ion and hydroxyl-ion.

Acidimetry and Alkalimetry. — When, as is constantly the case, a chemist desires to ascertain the **quantity** of an acid or base present in a solution, he uses for the purpose the interaction just

discussed. If, for example, the problem is to ascertain the weight of hydrogen chloride in each liter of a specimen of hydrochloric acid, this can be done by neutralizing a measured portion of this acid with a solution of an alkali of *known concentration*. The volume of the latter which is required for the purpose is observed.

A known volume of the acid is first measured out into a beaker by means of a pipette (Fig. 112) of fixed capacity, filled by suction to the mark on the stem. Suppose the amount to be 25 c.c. The standard alkali solution is placed in a burette (Fig. 113), which is filled down to the tip of the nozzle. A few drops of litmus solution are now added to the acid, and the alkali is allowed to run in slowly. After a time, the hydroxyl-ion which this introduces will begin to produce a blue color, close to where the stream enters the liquid. This is at first dissipated by stirring, and the litmus returns to red. Finally, however, a point is reached at which the entire solution assumes a tint intermediate between blue and red. With one drop less of the base, it is distinctly red. With one drop more, it would become distinctly blue. Litmus paper of either shade dipped in this neutral solution remains unaffected.

By the use of a standard solution of an acid in the burette, the concentration of a given alkali may be determined in the same way.

It is most important to note that the *activity* of acids and bases cannot be measured by the *quantity* of base or acid required to neutralize them. The full amount required by the equation is always needed in every case. This is because neutralization uses up the hydrogen- or hydroxyl-ion *at once*, and so permits the rapid generation of a fresh supply. The concentration of one of these ionic materials can only be measured by some action which uses it up slowly or not at all, so that ionic double decompositions are excluded. In the action of metals on acids (p. 318), and in determining conductivity (p. 324), the consumption of these ions is slow, and hence the measurement can be made in these cases. Actions which consume no ions at all are also known, and are used in measuring activity (see pp. 583, 604).

When the acid or base is but little soluble in water, as when zinc hydroxide is treated with a dilute acid, one other link is added to the network of equilibria. The acid proceeds to interact with the small dissolved part of the base. As this is disposed of, solution goes on progressively and, through a train of equilibria:

$$Zn(OH)_2 \text{ (solid)} \leftrightarrows Zn(OH)_2 \text{ (dslvd)} \leftrightarrows Zn^{++} + 2OH^-,$$

the supply of hydroxyl-ion is maintained until all the molecules of the base, solid and dissolved, are used up and the action is completed. Heating hastens these, as it does all other changes.

If acid and base are alike insoluble, it saves time, if the production of the

salt is the ultimate object, to fuse the materials together at a high temperature.

Standard Solutions. — The **standard solutions** used in volumetric work are usually normal, and contain one equivalent weight of the alkali or acid in one liter of the solution. For more delicate work, decinormal ($N/10$) solutions may be employed. The concentration of such a solution is called its **titer,** and the operation of analyzing another solution by means of it, **titration.** The value of standard solutions lies in the fact that, when once the solution has been prepared, and the exact concentration adjusted by quantitative experiments, its use does not require any weighing, and the measurements of volumes involved can be carried out with great rapidity.

The **calculation of the result** is also simple. One liter of normal alkali contains 17.008 g. of available hydroxyl, and one liter of normal acid, 1.008 g. of available hydrogen (p. 201). Equal volumes of normal solutions will therefore exactly neutralize one another, 18.016 g. of water being formed by interaction of a liter of each. If, for the neutralization of the 25 c.c. of hydrochloric acid used above, 50 c.c. of normal alkali are required, the acid is twice-normal ($2\ N$). When 15 c.c. are required, the acid is $^{15}/_{25}$ or $^{3}/_{5}\ N$. If the actual weight of the acid in the latter case has to be calculated, we remember that there are 36.468 g. of hydrogen chloride in 1 liter of a normal solution, and therefore $36.468 \times {}^{3}/_{5} \times {}^{25}/_{1000}$ g. $= 0.547$ g. in 25 c.c. of a solution which is $^{3}/_{5}$-normal.

Methods of quantitative analysis in which standard solutions are employed are known as **volumetric** methods, and are much used by analysts and investigators. They occupy much less time than **gravimetric** operations, in which numerous weighings have to be made, and are often just as accurate. The substances, like litmus, by whose change of color the completeness of the action is made known, are called *indicators.*

Indicators. — Indicators are substances which, in presence of certain other substances, assume a very deep color, or change sharply from one deep color to another. Thus, **phenolphthalein** (see p. 235) is colorless in presence of acids (*i.e.*, hydrogen-ion), and red (when dilute, pink) in presence of alkalies (*i.e.*, hydroxyl-ion). **Litmus,** again, is red with acids, and blue with alkalies. The change of color depends upon a chemical interaction in each case, but since indicators are chosen for their strong coloration, the quantity of the acid

or base used up in changing the tint of the trace of the indicator is so small as to be negligible. Other common indicators are **methyl orange,** a complex organic compound which gives, in acid solution, a red, and in alkaline solution a yellow, color, and **Congo red,** the sodium salt of an acid of complex structure (see Dyes). In neutral or alkaline solutions this is red; with acids it turns blue.

In cases of extremely small ionization, the presence or absence of visible action on litmus may form another means (compare p. 318) of estimating activity. Thus, litmus is *easily* turned red by a decinormal solution of acetic acid or of any more active acid, but hydrogen sulphide, in a solution of the same molecular concentration, contains only one-twentieth as many hydrogen ions (p. 317), and affects litmus paper but slightly. Paper dipped in Congo red exhibits differences in the activity of acids by the different depths of the tints it assumes. For example, it is much less markedly affected by acetic acid than by sulphuric acid of the same concentration.

Trinitrobenzene $C_6H_3(NO_2)_3$, which is colorless in acid solution and deep-orange in presence of an active base, can be used to show different concentrations of hydroxyl-ion. Thus, with N-sodium hydroxide it gives a dark orange color, but with a $N/10$ solution light orange. With N-ammonium hydroxide it gives a very faint color and with a $N/10$ solution no color.

Hydrogen-Ion Concentration. — Since water itself is a weak electrolyte, its ionization equilibrium at any fixed temperature will be expressed by the relation: $[H^+]\cdot[OH^-]/[H_2O] = K$. The extent of the ionization is so very minute that $[H_2O]$, in all dilute aqueous solutions, may be regarded as constant. Thus we obtain the expression: $[H^+]\cdot[OH^-] = \text{constant}$, and experiment shows that at 25° this constant has the value of 10^{-14}. This is known as the **ion-product constant** of water.

In a solution where $[H^+]$ is normal, $[OH^-]$ will be 10^{-14}. In a solution where $[OH^-]$ is normal, $[H^+]$ will be 10^{-14}. In a neutral solution, $[H^+]$ and $[OH^-]$ will both be 10^{-7}.

The use of negative exponents is rather cumbrous in practice, and a new term, **pH,** has therefore been introduced to express these facts more simply. When we say that, for a given solution, pH $=1$, we mean that its hydrogen-ion concentration is 10^{-1}. *The pH value is the exponent of the hydrogen-ion concentration with the negative sign omitted.* Thus, for a neutral solution, pH $= 7$.

The indicators used in volumetric analysis do not all change color at the true neutral point. For each, however, the limits within which the color change occurs have been carefully determined, in order that for any particular titration the experimental error may be reduced to a minimum by choosing the most suitable indicator.

Litmus does turn from red to blue approximately at pH = 7, but the color change is rather gradual, and litmus consequently gives a reliable end-point only for the titration of a strong acid against a strong base. Phenolphthalein begins to show a red color only when the solution is slightly basic (at about pH = 8), and gives most accurate results when a weak acid is titrated against a strong base. Methyl orange, on the other hand, does not start to change to red until the solution is on the acid side (at about pH = 4), and is most useful for titrating a strong acid against a weak base.

Other indicators or dyes are known which change color at every pH value from 0 to 14. Charts have been made, indeed, which show the exact shades of different indicators for each variation of 0.2 in pH throughout the whole range, and it is thus possible to determine the approximate hydrogen-ion concentration of any solution very rapidly by colorimetric methods.

The Part Played by the Solvent in Ionization. — So far, we have regarded water as playing (except in neutralization) merely a passive, physical rôle in aqueous solutions of electrolytes. The ions in a solution of hydrogen chloride, for example, have been regarded as simply H^+ and Cl^-, the solvent not being itself directly concerned in their formation or reactions.

This view, although sufficient for many purposes, will not stand strict investigation. Thus we know by experiment that the ions, when they migrate with the electric current in electrolysis, carry water with them. This indicates that ions are *hydrated.* The solvent is therefore *chemically active* in ionization. In ordinarily dilute aqueous solutions, the excess of solvent is so great that the portion removed by combination with the solute is negligible, and the simple method of considering ionic equilibria adopted in preceding paragraphs is substantially valid. Strictly speaking, we should write all ions in their hydrated forms (*e.g.*, $Cu(H_2O)_x^{++}$ for cupric ion in aqueous solution, instead of Cu^{++}, see p. 782), but in order to avoid complicating the equations the action of the solvent is generally omitted. In one important class of ionic reactions, nevertheless, namely those which represent **hydrolysis,** the water must be taken into careful consideration, as we shall discuss in detail in a later chapter (pp. 406–9).

Recent work, indeed, suggests that the distinction drawn between solvent and solute in explaining ionization phenomena is entirely misleading. Pure liquefied hydrogen chloride is practically a non-conductor, just like pure

water. It is quite an arbitrary procedure, therefore, to ascribe all of the conducting power of a mixture of hydrogen chloride and water to the former substance, and to regard the latter as quite inert.

The Swiss chemist, Werner, felt so strongly on this question that he went to the other extreme, regarding *water* as the *only ionizing substance* in solutions of this type! According to Werner's theory of acids and bases, an acid was a substance which combined with hydroxyl-ion, a base a substance which combined with hydrogen-ion. The dissociation equilibrium of water: $H_2O \rightleftharpoons H^+ + OH^-$, ordinarily preponderant towards the undissociated molecule, would be disturbed by the formation of stable complex ions such as $[HCl(OH^-)]$ and $[NaOH(H^+)]$, and a highly conducting solution would result. Werner's theory may seem strange at first glance to those accustomed only to the orthodox point of view, but it really leads to exactly the same results. We all agree that ions such as chloride-ion and sodium-ion are hydrated in aqueous solution, and there is evidently no fundamental difference between hydrated chloride-ion $[Cl^-(H_2O)]$, and "solvated" hydroxyl-ion $[HCl(OH^-)]$, or between hydrated sodium-ion $[Na^+(H_2O)]$ and "solvated" hydrogen-ion $[NaOH(H^+)]$. But it is obviously more logical to take both components of a conducting solution equally into consideration than to emphasize one and neglect the other entirely.

Now experiment shows that extensive *ionization* in solution always accompanies extensive *compound formation* on admixture. When no interaction at all between the components occurs, the solution is non-conducting. All strong acids, for example, give hydrates with water which are sufficiently stable to be isolated in the solid state. No very weak acids give isolable hydrates. Those mercuric salts which are highly ionized, as mercuric nitrate $Hg(NO_3)_2$, all yield hydrates, such as $Hg(NO_3)_2,8H_2O$. Those which are only slightly ionized are all non-hydrated. It is possible, therefore, to regard ionization as due to the formation of solvent-solute complexes. The attractive forces between the constituent groups in such complexes would be considerably weaker than in the simpler molecules of the two components, and disintegration into free oppositely-charged radicals could occur much more readily.

The Modern Theory of Acids and Bases. — The function of the solvent in ionization is particularly interesting in the case of acids. Although it is customary to regard the properties of an acid as the properties of hydrogen-ion (p. 318), it is certain that the simple ion H^+ is incapable of existence in aqueous solution. As will be explained in a later chapter (p. 472), a hydrogen atom which has lost an electron and thereby become a positively-charged hydrogen-ion consists of a single **proton,** or positive unit of electricity. The volume of the proton, however, is almost infinitesimally small (see p. 479), and such a minute electrically-charged particle would exercise such an intense attractive force on any molecule of water in its vicinity as to result, inevitably, in the formation of the very stable **oxonium-ion** H_3O^+. This is exactly analogous to ammonium-ion NH_4^+, formed by the union of hydrogen-ion with NH_3 in a solution containing free ammonia.

In other solvents in which acids form conducting solutions the so-called hydrogen-ion will also, in point of fact, be similarly solvated, the true positive ion in the solution being a solvent molecule which has combined with a proton. An *acid* may be defined, consequently, as a *donor of protons*. Water itself is an acid according to this definition, as may be seen from its reaction with ammonia:

$$NH_3 + H_2O \leftrightarrows NH_4^+ + OH^-.$$

Conversely, a *base* may be defined as an *acceptor of protons* — a much more general definition than our previous one which merely regarded the properties of a base as the properties of hydroxyl-ion (p. 293). Water, ammonia, and the anion of any weak acid (for details, see pp. 406–9, 754) are all bases under this definition.

Exercises. — 1. For the neutralization of 77 c.c. of a certain alkaline solution, 25 c.c. of normal hydrochloric acid are required. What is the concentration of the alkali (p. 337)? If the alkali was sodium hydroxide, what weight of the substance was present? If the alkali was barium hydroxide, what weight of it was present?

2. Formulate (p. 332) the neutralization of acetic acid by ammonium hydroxide.

3. What volume of 0.1 N sodium hydroxide will be required to neutralize (*a*) 10 c.c. of 0.1 N hydrochloric acid, (*b*) 10 c.c. of 0.1 N acetic acid? Which of the two acid solutions contained the higher concentration of hydrogen-ion (p. 317)? Can you reconcile your answer with the results you have just obtained?

4. Is it correct to call a 10 N solution of acetic acid in water a *strong* solution, or a 0.001 N solution of hydrochloric acid a *weak* solution? Give reasons and, if you disagree, suggest alternatives.

5. A normal solution of hydrochloric acid is apparently 78 per cent ionized; a deci-normal solution is apparently 92 per cent ionized. Which of the two solutions, when filling the glass trough in the apparatus shown in Fig. 111 (p. 324), will show the lower resistance? Reconcile your answer with the results obtained on p. 324.

6. Each of four wide glass tubes is fitted up as follows: The lower end is closed tightly with a two-holed rubber stopper, through which pass an electrode and a small tube with stop-cock and nozzle. The upper end is also plugged with a two-holed stopper through which pass loosely a long narrow tube enclosing a second electrode and a funnel for use in filling the tube. The four tubes are fixed upright on a board side by side, and each is connected up with a direct-current circuit and a signal lamp (pp. 294–5). The tubes are now filled with normal solutions of (*a*) hydrochloric acid, (*b*) acetic acid, (*c*) sodium hydroxide, and (*d*) ammonium hydroxide respectively. What do you observe when the circuit is completed, the upper electrode remaining near the top of the tube in each case? Explain. What do you observe as the upper electrodes in (*b*) and (*d*) are pushed down towards the lower electrodes? Explain.

7. One-half of the solution filling each of the tubes in Exercise 6 is withdrawn. The part withdrawn from (*c*) is added to (*a*), and the part withdrawn from (*d*) is added to (*b*). How is the conductivity of the solution affected in each case? Explain by formulating the reactions in detail.

8. Will the concentration of hydrogen-ion in pure water increase or decrease with rise of temperature? [*Hint:* Apply Le Chatelier's Law to the equation on p. 333.]

9. From the solubility data on the inside front cover, devise two other experiments where the mixture of solutions of two soluble salts leads to a *double* precipitation. Formulate each case in detail.

10. The following data represent the changes in the ionized fraction of acetic acid with concentration at 18°. Concentrations are expressed in normalities.

Total concentration of acid	1.0	0.1	0.01
Percentage of acid ionized	0.41	1.30	4.07

Calculate from these figures, for each solution, in terms of normalities: (*a*) the concentration of hydrogen-ion H^+ and acetate-ion $CH_3.COO^-$, and (*b*) the concentration of undissociated acetic acid $CH_3.COOH$.

11. Calculate, finally, the value of the expression: $[H^+]\cdot[CH_3.COO^-]/[CH_3.COOH]$ for each solution. Does the ionization equilibrium of acetic acid at 18° vary in accordance with the law of molecular concentration (p. 273)?

12. Compare the value found above for 18° with that at 25° (p. 327). Is heat absorbed, or evolved, in the ionization of acetic acid (see p. 325)?

13. Why would methyl orange not give a sharp end-point for the titration of a weak acid against a strong base?

14. Why is it impossible to titrate accurately a weak acid against a weak base, whatever the indicator used?

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CHAPTER XX

THE HALOGEN FAMILY

The elements, if we may judge from those studied or mentioned thus far, may be divided into two classes — the metallic or positive elements, like sodium, zinc and magnesium, and the non-metallic or negative elements, like oxygen, chlorine and sulphur. The former give positive ions, such as Na^+, Mg^{++}. The latter give negative ions, such as Cl^-, $S^=$. Hydrogen constitutes the single exception, giving the *positive* ion H^+.

Natural Families of Elements. — We have a simple means of subdividing *within* each of these two classes. We can place together the elements of like chemical behavior. Thus, among univalent positive elements, sodium and potassium, and, among bivalent positive elements, zinc and magnesium resemble one another very closely in their reactions. Also, oxygen and sulphur form one group and chlorine, bromine, iodine and fluorine form another. Groups of this kind are often spoken of as **natural families** of elements. The last group is called the **halogen family,** from the Greek for *salt-producing,* because these elements combine with sodium to give substances all resembling common salt. Usually, the elements of one family and their corresponding compounds resemble one another in a number of ways, and show at the same time a gradation in properties which it is interesting to study.

The elements to which we have so far devoted most attention have been oxygen, hydrogen, and chlorine. If we recall the chemical properties and relations of these elements we shall recognize the fact that they all possess very distinct individualities. If all the other chemical elements differed from one another as much as do these three, the study of their chemical relations would be tedious and tiresome, since we should be denied the satisfaction of tracing resemblances, and the elements would be incapable of classification. In reality, however, we find that they are all capable of being grouped together in sets. In some families the resemblance is close, in others less close. The present group is of the former class, and will serve, therefore, as a convenient beginning in the work of tracing relations between the elements and in classifying the facts of descriptive chemistry.

BROMINE Br_2

The element was discovered by Balard in 1826 and derives its name from its offensive odor (Greek, *a stench*).

Preparation. — Many salt deposits and natural salt wells contain some bromides, along with large quantities of common salt. When the bulk of the latter has been separated by evaporation and crystallization, the bromides of sodium and magnesium, which are more soluble, collect in the mother liquor.

Free bromine can be liberated at the positive electrode by elec-

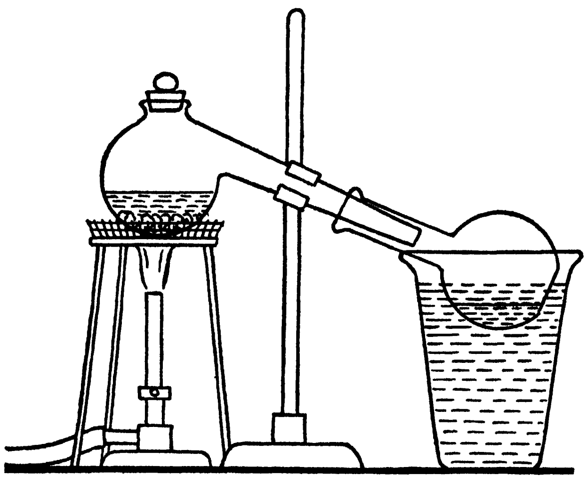


FIG. 114. Preparation of Bromine.

trolysis of this mother liquor (compare p. 238), but usually a chemical process is employed.

In one process, chlorine gas is dissolved in the liquor. This *displaces* the bromine, and the latter can be distilled out by heating:

$$2Br^- + Cl_2 \rightarrow 2Cl^- + Br_2.$$

In another process, *oxidation* of the bromide-ion Br^- by pulverized manganese dioxide and sulphuric acid is employed, and this method can be used in the laboratory (Fig. 114).

The manganese dioxide is reduced to manganese sulphate (compare p. 241), its oxygen combining with hydrogen from H_2SO_4 to

form water. The sodium bromide used is converted to sodium hydrogen sulphate (compare p. 225) and bromine is liberated.

Skeleton:
$NaBr + MnO_2 + H_2SO_4 \rightarrow Br_2 + NaHSO_4 + MnSO_4 + H_2O.$

Balanced:
$2NaBr + MnO_2 + 3H_2SO_4 \rightarrow Br_2 + 2NaHSO_4 + MnSO_4 + 2H_2O.$

The beginner will doubtless find it difficult to balance the above equation by himself, since the method formerly recommended (p. 81) is not readily adapted to reactions in which several initial substances or products are involved, particularly when (as happens in this case) changes of valence on the part of certain elements also occur in the course of the reaction. Rules for his assistance in working out this and similar complex equations will be presented in the following chapter.

Although sea-water contains bromine (in the form of sodium bromide) to an extent of less than 70 parts per million, it is possible to extract even this small proportion successfully on a commercial scale. The first method employed involved the addition of aniline (p. 587) to chlorinated sea-water, the insoluble tribromoaniline being precipitated:

$$3NaBr + 3Cl_2 + C_6H_5NH_2 \rightarrow C_6H_2Br_3NH_2 + 3NaCl + 3HCl.$$

The process now developed at a plant on the coast of North Carolina consists of four stages: (*a*) treating slightly-acidified sea-water with chlorine to liberate the bromine, (*b*) blowing the free bromine out of solution with air (see p. 219), (*c*) absorbing the bromine vapor from the air with sodium carbonate solution:

$$3Na_2CO_3 + 3Br_2 \rightarrow 5NaBr + NaBrO_3 + 3CO_2,$$

(*d*) acidifying the bromide-bromate liquor with sulphuric acid:

$$5NaBr + NaBrO_3 + 3H_2SO_4 \rightarrow 3Na_2SO_4 + 3Br_2 + 3H_2O.$$

The bromine obtained (15,000 pounds per day) is converted into ethylene dibromide $C_2H_4Br_2$ for use in conjunction with tetra-ethyl lead $Pb(C_2H_5)_4$ in the treatment of gasoline motor fuel (see p. 830).

Properties. — Bromine is a liquid of a deep red-brown *color* and the vapor, of the same color, has a suffocating *odor*. It *boils* at 59°, and even at ordinary temperatures gives a high vapor pressure (150 mm. at 18°) and evaporates quickly when exposed to the air. When cooled it forms red, needle-shaped crystals, which

melt at —7.3°. It is moderately *soluble* in water, giving a 3.2 per cent solution **(bromine-water),** and is very soluble in carbon disulphide. The *density* of the vapor gives it the formula Br_2.

Great care must be used in handling bromine, as, when spilt upon the skin, it kills the tissues and the sore is very liable to become infected. Burns made by bromine or concentrated acids should be washed instantly with water and then with bicarbonate of soda solution, and covered thickly with vaseline, or a salve of boric acid in lanoline, to protect them from infection.

A jet of burning *hydrogen* will continue to burn in bromine vapor, giving hydrogen bromide, a gas which fumes in moist air like hydrogen chloride:

$$H_2 + Br_2 \rightarrow 2HBr.$$

Many of the *metals,* when thrown in the form of powder, leaf, or foil, into bromine vapor, combine directly, giving bromides. The action is similar to that with chlorine, but less vigorous. Some of the non-metals, like phosphorus and arsenic, also burn in bromine vapor.

Hydrogen Bromide HBr. Preparation. — Hydrogen and bromine vapor unite much less readily than hydrogen and chlorine. A stream of pure hydrogen bromide is most easily made by moistening red phosphorus with water, and allowing bromine to fall drop by drop into the paste (Fig. 115). To absorb the bromine vapor, carried by the gas, the latter is passed through a **U**-tube containing dry red phosphorus mixed with broken glass or beads:

$$2P + 3Br_2 \rightarrow 2PBr_3.$$
$$PBr_3 + 3H_2O \rightarrow 3HBr \uparrow + H_3PO_3.$$

The bromine first combines vigorously with the phosphorus to form phosphorus tribromide, which is immediately decomposed (or *hydrolyzed,* see p. 231) by the water. The phosphorous acid H_3PO_3 remains, dissolved in the water, in the flask. The second **U**-tube, containing water, may be attached when a solution of the gas is required. If it is omitted, the gas can be collected in a jar by upward displacement of air.

It might seem that a simpler action would be that of sulphuric acid upon a bromide (compare p. 225):

$$H_2SO_4 + KBr \rightarrow KHSO_4 + HBr \uparrow.$$

This action does take place, but the hydrogen bromide formed, being less stable than HCl, is oxidized rapidly by the concentrated sulphuric acid, so that, although some of the gas escapes oxidation, it is mixed with much free bromine and sulphur dioxide: $H_2SO_4 + 2HBr \rightarrow SO_2 + 2H_2O + Br_2$. This action, indeed, enables us to *recognize* a bromide, by the color of the bromine vapor and the fuming of the hydrogen bromide produced.

Since all acids decompose all salts more or less (p. 292), by use of an acid which does not give up its oxygen so readily, such as phosphoric acid, pure hydrogen bromide may be obtained ($KBr +$

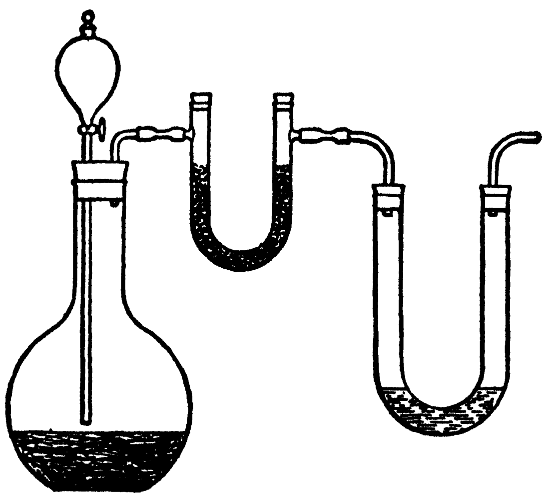


FIG. 115. Preparation of Hydrogen Bromide.

$H_3PO_4 \rightarrow HBr + KH_2PO_4$). The small solubility of the salt in concentrated phosphoric acid retards the interaction (p. 280) and makes the evolution of the gas very slow, however.

In connection with this topic of methods of preparation, the student should be warned that *a method which works on paper is not necessarily good in practice.* Every class contains members who *insist* on preparing HBr or HI as follows:

$$NaBr + HCl \rightarrow NaCl + HBr. \qquad (1)$$

The idea behind this method is that, inasmuch as chlorine can displace bromine or iodine from combination, as expressed by the reaction:

$$2Br^- + Cl_2 \rightarrow Br_2 + 2Cl^- \qquad (2)$$

the same scheme ought to work for the hydrogen halides. But two things have been forgotten. The first is that *it is only free chlorine that can displace bromine,* and in equation (1) we have no free chlorine. The second is, that even although reaction (1) does take place to some extent, it is a *typical double decomposition, and as such it is reversible.* Now we can drive a reacaction of this type to completion only by separating one of the products as a gas, a precipitate, or a non-ionized substance. The second and third devices are not available in this case, since all of the substances are very soluble and highly ionized in water. As regards the first method, it is true that, if we boil the solution, we shall get some hydrogen bromide distilling over, but it will be mixed with hydrogen chloride, since that is also volatile. As a means of obtaining pure HBr, therefore, reaction (1) is absolutely useless.

Physical Properties of Hydrogen Bromide. — Hydrogen bromide is a colorless gas with a sharp odor. It is two and a half times as heavy as air (molar weight, 81 g.). It is easily reduced to the liquid condition (b.-p. — 69°). It is exceedingly soluble in water, and in contact with moist air condenses the water vapor to a fog of liquid particles. When distilled, the solution in water behaves like that of hydrogen chloride (p. 228). It loses mainly either water or hydrogen bromide, according as it is dilute or exceedingly concentrated, until an acid of constant boiling-point (126° at 760 mm. pressure), containing 48 per cent of hydrogen bromide, passes over. Pure hydrogen bromide, whether in the gaseous condition or in the liquefied form, is a nonconductor of electricity.

Chemical Properties of Hydrogen Bromide. — The chemical properties of hydrogen bromide are similar to those of hydrogen chloride (p. 229). It is somewhat less stable, and dissociation into its constituents begins to be noticeable at 800°. When free from water, it is not an acid (see below). The gas interacts vigorously with chlorine, hydrogen chloride and free bromine being produced, and much heat is evolved by the change, $2HBr + Cl_2 \rightarrow 2HCl + Br_2$.

Chemical Properties of Hydrobromic Acid. — The solution of hydrogen bromide in water is a strong acid (see p. 318). It conducts electricity extremely well. In contact with active metals, and with oxides of metals and hydroxides of metals, it behaves exactly like hydrochloric acid (p. 229). In the first case, hydrogen is set free and the bromide of the metal is produced. In the two other cases, water and the bromides of the metals are produced. For example:

$$Zn(OH)_2 + 2HBr \rightarrow ZnBr_2 + 2H_2O.$$

As an *acid,* hydrobromic acid gives double decompositions with

bases and salts. Thus, with a salt of silver, we get a cream-colored precipitate of insoluble silver bromide:

$$AgNO_3 + HBr \rightarrow AgBr \downarrow + HNO_3.$$

Chlorine-water, added to a solution of any bromide, displaces the bromine, which may be recognized by its brown color (**test for a** bromide):

$$Cl_2 + 2Br^- \rightarrow 2Cl^- + Br_2.$$

A few drops of carbon disulphide, shaken with the mixture, will settle to the bottom, carrying the brown bromine with it in a more concentrated, easily recognizable form (compare p. 220).

Oxidizing agents, such as manganese dioxide MnO_2, also liberate bromine from hydrobromic acid (compare p. 240).

Uses of Compounds of Bromine. — Bromine is manufactured in large amounts in Germany and in the United States. Its chief use is in the production of ethylene dibromide (see p. 585). It is employed also to make potassium bromide and other bromides. These are utilized as sedatives in medicine, and to precipitate silver bromide in the manufacture of photographic films and plates. Bromine is also required in large quantities in the manufacture of intermediate products used in the preparation of organic dyes.

IODINE I_2

Sources. — Iodine was formerly all obtained from seaweed (kelp), certain species of which use the traces of organic compounds of iodine in sea water as part of their food. The dried seaweed is carbonized in retorts, and sodium iodide remains in the residue, along with much sodium carbonate and carbon. In an improved process the iodine compounds are dissolved out of the kelp, and from the latter a sort of gelatine, named **algin,** is extracted.

The greater part of our supply of iodine is at present obtained from sodium iodate $NaIO_3$, which forms about 0.2 per cent of crude Chile saltpeter (see p. 504).

Preparation. — The processes for obtaining iodine from an iodide are precisely the same as those for bromine from a bromide.

In France chlorine is used to displace the iodine:

$$Cl_2 + 2I^- \rightarrow 2Cl^- + I_2 \downarrow.$$

The precipitate of iodine is pressed from the solution.

In Great Britain the iodide is mixed with manganese dioxide and sulphuric acid and heated:

$$3H_2SO_4 + MnO_2 + 2NaI \rightarrow MnSO_4 + 2NaHSO_4 + 2H_2O + I_2 \uparrow .$$

Iodine vapor condenses upon a cold surface, not to the liquid, but directly to the solid, crystalline form. Distillation which gives a solid product is called **sublimation.** The crude iodine is purified by repetition of this process.

An important recent development is the treatment of the oil-well brines of Southern California (which contain from 30 to 70 parts per million of iodine in the form of sodium iodide) either with an acidified solution of sodium nitrite $NaNO_2$:

$$2NaI + 2H_2SO_4 + 2NaNO_2 \rightarrow 2Na_2SO_4 + 2H_2O + 2NO + I_2,$$

or with a solution of silver nitrate, which precipitates the highly-insoluble silver iodide.

Physical Properties. — Iodine (Greek, *like a violet*) is a black, solid substance (sp. gr. 5), exhibiting large crystalline plates of rhombic form. It melts at 114°, and boils at 184°. The vapor has at first a reddish-violet tint, and on being more strongly heated becomes deep blue (see next section).

Iodine is very slightly soluble in water (about 1 : 6000), and the solution has a scarcely perceptible brown tint. It is much more soluble in carbon disulphide and in chloroform (p. 220), in which it gives violet solutions. In alcohol it gives a solution which is brown, the iodine being in a condition of feeble combination, and not simply in solution. An aqueous solution of potassium iodide, hydrogen iodide, or any other iodide, has likewise the power to take up large quantities of iodine. Here the formation of definite compounds by a reversible action (such as $KI + I_2 \rightleftarrows KI_3$), accounts for the amount of iodine taken up.

The behavior of free iodine towards starch forms a distinctive *test* for both substances (see p. 7). The pale-brown aqueous solution, for example, when added to starch emulsion, produces a deep-blue color. This blue substance is not a chemical compound. The iodine is adsorbed by the starch, which is in colloidal suspension (see p. 198).

Chemical Properties. — The molecular weight of iodine, ascertained by weighing the vapor at temperatures from the boiling-point up to 700°, is 253.8. The atomic weight being 126.92, the

molecule contains two atoms. Beyond 700°, the vapor diminishes in density more rapidly than Charles' law would lead us to expect, and at 1700° the molecular weight has fallen to 127 (see p. 194). As the vapor is heated, a larger and larger proportion of the molecules is broken up, until the decomposition has become complete. As in all cases of dissociation, when the vapor is cooled the atoms recombine to form molecules. This is the most notable case in which we encounter both the monatomic and the diatomic forms of the same element. The heat given out when the atoms reunite to form the molecules is very considerable ($2I \rightleftarrows I_2 + 28{,}500$ cal.), indicating that the chemical union of two atoms of identical nature may be as vigorous as that of two atoms of different chemical substances. The heat of union of atomic hydrogen (p. 190) is even greater ($2H \rightleftarrows H_2 + 100{,}500$ cal.). In both cases, in accordance with Van't Hoff's law (p. 284), raising the temperature increases the dissociation, because that is the direction in which heat is absorbed.

Iodine *unites* very slowly with hydrogen, even when heated. It unites directly with some non-metals and with the majority of the metals. When phosphorus is presented in the white form (see p. 232), the action takes place spontaneously without the assistance of heat. Both chlorine and bromine *displace* iodine from combination with hydrogen and the metals ($2HI + Br_2 \rightarrow 2HBr + I_2$).

Iodine in water, like chlorine in water (p. 245), constitutes an oxidizing agent, although the former is much the feebler of the two. The hypo-iodous acid, formed in minute amounts at a time, converts sulphurous acid (p. 174) into sulphuric acid:

$$I_2 + H_2O \rightleftarrows HI + HOI.$$
$$HOI + H_2SO_3 \rightarrow HI + H_2SO_4.$$

In analytical chemistry a solution of iodine in potassium iodide, containing a known proportion of dissolved iodine (a **standard** solution), is used for estimating the quantity of an oxidizable substance present in a given specimen. The amount of oxidizable substance present is measured by the quantity of the standard iodine solution which can be decolorized when run in from a burette (see p. 336). This method is known as **iodimetry.**

The Direct Union of Hydrogen and Iodine. — The slow union of hydrogen and iodine referred to above, giving hydrogen iodide, is a reversible reaction:

$$2HI \rightleftarrows H_2 + I_2.$$

That is to say, whether we charge a tube with hydrogen iodide, or with an equal amount of the elements in the correct proportions by

weight, if we place both tubes in a bath, and keep them thus at the same temperature, the contents of the tubes will after a time be identical (p. 274).

At 283°, a mixture of hydrogen and iodine yields 83 per cent of hydrogen iodide and 17 per cent of the uncombined elements. At 445°, the yield of hydrogen iodide is 80 per cent, and at 508° only 76 per cent. Since the free elements increase in quantity as the temperature rises, we infer (see p. 284) that the dissociation of the compound *absorbs heat.* Change of pressure does not affect the point of equilibrium (see p. 277).

Hydrogen Iodide HI. Preparation. — The gas is most conveniently prepared by a process similar to that employed in the case of hydrogen bromide (Fig. 115, p. 347). Red phosphorus and iodine are mixed, and water is allowed to fall drop by drop upon the mass:

$$2P + 3I_2 \rightarrow 2PI_3.$$
$$PI_3 + 3H_2O \rightarrow 3HI + H_3PO_3.$$

The action of sulphuric acid upon an iodide does **not** give pure hydrogen iodide, although the action $NaI + H_2SO_4 \rightarrow NaHSO_4 + HI$ does take place (compare p. 347). Hydrogen iodide, being much less stable than even hydrogen bromide, is a more active reducing agent, and reduces the sulphuric acid to hydrogen sulphide. The odor of this gas is therefore very conspicuous when an iodide is moistened with sulphuric acid:

$$H_2SO_4 + 8HI \rightarrow H_2S + 4H_2O + 4I_2.$$

The violet vapor of iodine becomes visible if the test-tube is warmed. A rough **test** for an iodide is afforded by this action.

Powdered sodium iodide and concentrated phosphoric acid (see p. 347), when warmed, give pure hydrogen iodide very slowly: $NaI + H_3PO_4 \rightleftarrows HI\uparrow + NaH_2PO_4$. This action was formerly used in preparing the gas.

Another method of making hydrogen iodide is frequently employed when a solution of the gas in water is required, and not the gas itself. Powdered iodine is suspended in water, and hydrogen sulphide gas is introduced through a tube in a continuous stream. The iodine dissolves slowly in the water and acts by displacement upon the minute amount of sulphide ion $S^{=}$, derived from the solution of H_2S in water. Sulphur separates in a fine powder, the

H_2S progressively dissociates into $2H^+$ and $S^=$, and a solution of hydrogen iodide (hydriodic acid) is formed:

$$S^= + I_2 \rightarrow 2I^- + S\downarrow.$$

The solution is freed from the deposit of sulphur by filtration, and may be concentrated to 57 per cent of hydriodic acid by distilling off the water.

The theory of the last method is worthy of attention. It will be seen that while iodine has little tendency to unite with free hydrogen, it is here able to decompose a compound containing hydrogen, in order to secure this element. It is enabled to do this by the fact that the very large amount of heat given out by the solution of hydrogen iodide in water converts the action, which would otherwise be endothermal, into an exothermal one. In the absence of water the reverse of the above action takes place with ease (p. 403). In presence of water, however, the great heat of solution (p. 210) of the hydrogen iodide (+ 19,200 cal.) more than balances the heat absorbed by the chemical change, and the action as a whole takes place with evolution of heat.

Physical Properties of Hydrogen Iodide. — Hydrogen iodide is a colorless gas with a sharp odor. Its molecular weight is 128 and it is therefore much heavier than air, the average weight of whose molecules is 28.955 (p. 185). It is a nonconductor of electricity, both in the gaseous and in the liquefied conditions. It is exceedingly soluble in water, so that at 10° 30 grams of water will absorb 70 grams of the gas. The behavior of this solution is similar to that of hydrogen chloride and hydrogen bromide (see p. 228). The mixture of constant boiling-point distils over at 127° (at 760 mm.), and contains 57 per cent of hydrogen iodide.

Chemical Properties of Hydrogen Iodide. — Hydrogen iodide is the least stable of the hydrogen halides. When heated it begins visibly to decompose into its constituents at 180°. On account of the ease with which it parts with the hydrogen which it contains, it can be burned in oxygen gas, $4HI + O_2 \rightarrow 2H_2O + 2I_2$. When the gas is mixed with chlorine, a violent chemical change, accompanied by a flash of light, occurs, the iodine is set free, and hydrogen chloride is produced, $Cl_2 + 2HI \rightarrow 2HCl + I_2$. Bromine vapor will similarly displace the iodine from hydrogen iodide.

Chemical Properties of Hydriodic Acid. — In most respects the aqueous solution behaves exactly like hydrochloric and hydrobromic acids. With oxidizing agents, for example, such as manganese dioxide, it readily gives free iodine, just as the others (pp. 240,

349) give free chlorine and bromine, respectively. Here, however, the oxidation is so much more easily carried out, that it is slowly effected by atmospheric oxygen, so that hydriodic acid left exposed to the air gradually becomes brown ($O_2 + 4HI \rightarrow 2H_2O + 2I_2$).

On account of the ease with which hydriodic acid parts with its hydrogen, it is frequently used in chemistry as a reducing agent.

The iodide-ion I^-, which hydriodic acid contains, gives, with any soluble salt of silver, a precipitate of insoluble yellow silver iodide AgI:

$$AgNO_3 + HI \rightarrow AgI\downarrow + HNO_3.$$

Chlorine-water or bromine-water, added to a solution of hydriodic acid or any other iodide, displaces the iodine:

$$Br_2 + 2I^- \rightarrow 2Br^- + I_2.$$

The free iodine, even if present in minute amounts, may be *recognized* by shaking the liquid with a few drops of carbon disulphide. The iodine gives a violet solution in the latter. A still more delicate *test* is the addition of a drop of very thin starch paste, which gives a deep-blue tint with *free* iodine (see p. 350). Filter paper dipped in starch paste and dried can also be used, by touching it with a drop of the solution containing the free iodine.

Uses of Iodine and Its Compounds. — The alcoholic solution (tincture of iodine), painted over the skin, reduces swellings and inflammation. **Iodoform** CHI_3 is a solid used for similar purposes. **Thyroxin** $C_{15}H_{11}O_4NI_4$ is an organic compound found in the human thyroid gland, as well as in that of other animals. An extract of sheep's thyroids (or, still better, synthetically prepared thyroxin) is administered with remarkable success in cases of degeneration caused by abnormally small natural development of this gland (cretinism). Potassium iodide is also used in medicine, to cause absorption of blood-clots and effusions of blood, for example in the eye. Silver iodide is contained in the coating on photographic plates and films.

FLUORINE F_2

The discussion of this element should logically have preceded that of chlorine, since it of all the members of the halogen family is the most active. Chlorine was taken up first, however, because

its compounds are more familiar. Fluorine is found in nature chiefly in the minerals **fluorite** (calcium fluoride) CaF_2, and **cryolite,** a double fluoride of aluminium and sodium $AlF_3,3NaF$. It is found also in small amounts in bones (especially the teeth).

Preparation. — When a solution of hydrofluoric acid is heated with manganese dioxide, oxidation does not occur and free fluorine is not produced. For many years all efforts to isolate the element failed. It was perfectly understood that the reason of these failures lay in the greater chemical activity of fluorine, which made it more difficult to separate from any state of combination than the other halogens. Its preparation was finally achieved by Moissan (1886) by the decomposition of anhydrous hydrogen fluoride, which is liquid below 19°, by means of electricity. The apparatus (Fig. 116) is made of copper, which, after receiving a thin coating of the fluoride, is not further affected. To reduce the tendency to chemical union, the whole is immersed in a bath giving a temperature between —23° and —40°. The electrodes are made of an alloy of platinum and iridium, which is the only material that can resist the action of the fluorine. Hydrogen fluoride, like the other hydrogen halides (p. 339), is a non-conductor of electricity when pure, and a small quantity of potassium-hydrogen fluoride KHF_2 has to be added to enable the current of electricity to pass. The fluorine is set free at the positive electrode, and hydrogen appears at the negative.

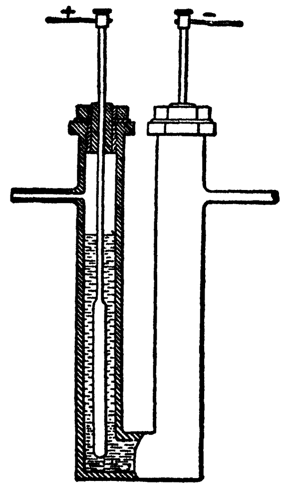


FIG. 116. Preparation of Fluorine.

A more recent, and easier, method for the preparation of fluorine is by the electrolysis of fused potassium-hydrogen fluoride (m.-p., 217°) in a copper vessel with graphite electrodes insulated in bakelite cement stoppers (see p. 652).

Properties. — Fluorine is a gas whose color is like that of chlorine, but somewhat paler. Its density (38) shows that the molecule is diatomic (F_2). The gas is the most difficult of the halogens to liquefy. The liquid boils at —187°.

Fluorine combines with every element, with the exception of the

members of the helium family (see pp. 462–4), and in most cases does so with such vigor that the union begins spontaneously without the assistance of external heat. Dry platinum and gold are the elements least affected. It explodes with hydrogen at the ordinary temperature, without the assistance of sunlight. On the introduction of ice-cold water into a tube of fluorine, the oxygen of the water is partially *displaced* by fluorine, the main products of the interaction being hydrogen peroxide (p. 366) and hydrofluoric acid: $F_2 + 2H_2O \rightarrow H_2O_2 + H_2F_2$.

Fluorine displaces the chlorine in hydrogen chloride as easily as chlorine in turn displaces bromine or iodine.

Fluorine oxide, a stable gas with the formula F_2O, has recently been prepared by passing a slow current of fluorine through a dilute solution of sodium hydroxide:

$$2F_2 + 2NaOH \rightarrow 2NaF + F_2O + H_2O.$$

Hydrogen Fluoride H_2F_2. Preparation. — Pure, dry hydrogen fluoride is best made by heating potassium-hydrogen fluoride, $2KHF_2 \rightleftarrows 2KF + H_2F_2 \uparrow$. For ordinary purposes, however, the preparation of an aqueous solution is the ultimate object. Usually, powdered calcium fluoride is treated with concentrated sulphuric acid, and the mixture distilled in a retort of platinum or lead:

$$CaF_2 + H_2SO_4 \rightleftarrows CaSO_4 + H_2F_2 \uparrow.$$

The hydrogen fluoride passes over and is caught in distilled water. The aqueous solution of hydrofluoric acid thus obtained has to be kept in vessels made of lead, rubber, or paraffin, as glass interacts with the acid with great rapidity (see p. 357).

Properties of Hydrogen Fluoride. — The vapor of hydrogen fluoride can be condensed to a colorless *liquid* boiling at 19.4°. Being very *soluble in water,* it fumes strongly in moist air. The vapor *density* around 40° corresponds roughly with the formula H_2F_2, but at higher temperatures gradual dissociation to HF occurs.

Recent investigations have thrown considerable doubt on the existence of the molecular species H_2F_2 in hydrogen fluoride gas, the abnormal vapor density values being ascribed to the presence of still more highly associated complexes (such as H_4F_4 and H_6F_6) in a state of partial dissociation. The stability of the acid salts KHF_2 and $NaHF_2$ points very strongly, however, towards a parent substance with the formula H_2F_2, and this formula may therefore be retained until more decisive evidence on the question is produced.

Association. — Many substances resemble hydrogen fluoride in consisting of mixtures of molecules which are multiples of the simplest possible. Thus, acetic acid vapor at the boiling-point has the formula $(CH_3,COOH)_2$, and sulphur vapor at high temperatures is S_2 (p. 194), but at lower temperatures a mixture of S_2, S_6, and S_8. These are **associated vapors.**

There are also **associated liquids.** Thus, sulphuric acid and nitric acid in the liquid condition are composed of more complex aggregates than H_2SO_4 and HNO_3. Water is essentially highly associated $(H_2O)_n$, although the vapor is H_2O (p. 204). In all such cases *dissociation* into the simpler molecules takes place *gradually* as the temperature is raised.

Many substances, however, naturally possess formulæ which are multiples of the simplest without showing, as the temperature is raised, any tendency to progressive dissociation into the corresponding simplest molecules. Thus, acetylene (p. 191) is C_2H_2 at all temperatures, and acetic acid (p. 191), although it is associated to $C_4H_8O_4$ at its boiling-point, never becomes simpler than $C_2H_4O_2$ at any temperature.

When a substance changes *sharply* into another substance with double or triple molecular weight, as formaldehyde CH_2O, a volatile liquid, changes into paraformaldehyde $(CH_2O)_3$, a crystalline solid, the phenomenon is not called association, but **polymerization.**

Properties of Hydrofluoric Acid. — The aqueous solution of hydrogen fluoride has all the properties of a *transition acid* (see p. 318). Metals like zinc and magnesium interact with hydrofluoric acid with evolution of hydrogen, although the action is less violent than with other halogen acids. The acid interacts with oxides and hydroxides, forming fluorides (p. 230). The chief difference in this respect which it exhibits, when compared with the other halogen acids, is the one which leads us to assign to it the formula H_2F_2. We may displace either one or both the hydrogen atoms in the molecule with a metal. Thus, one of the commonest salts of hydrofluoric acid is potassium-hydrogen fluoride KHF_2, mentioned above: $KOH + H_2F_2 \rightarrow KHF_2 + H_2O$. In this respect the acid resembles sulphuric acid and other acids containing more than one replaceable hydrogen unit. Unlike the other halogen acids, hydrofluoric acid gives **acid salts** (p. 291) with great ease.

The most remarkable property of hydrofluoric acid is that it interacts readily with sand (silicon dioxide SiO_2) giving silicon tetrafluoride SiF_4 (a gas) and water:

$$SiO_2 + 2H_2F_2 \rightarrow SiF_4 \uparrow + 2H_2O.$$

No other acid is able thus to act upon the oxide of a typical non-metallic element. In fact, in all other cases (*e.g.*, $SiCl_4$), water decomposes the halide (hydrolysis), and the action goes in the opposite direction.

Glass, which is commonly made by fusing together sodium carbonate, calcium carbonate, and sand (see p. 661), is a mixture of silicates of calcium and sodium, and is rapidly decomposed by hydrofluoric acid. The nature of the change is shown by the two following equations:

$$CaSiO_3 + 3H_2F_2 \rightarrow SiF_4 \uparrow + CaF_2 + 3H_2O.$$
$$Na_2SiO_3 + 3H_2F_2 \rightarrow SiF_4 \uparrow + 2NaF + 3H_2O.$$

All other silicates are decomposed according to the same plan. The silicon tetrafluoride passes off. The fluorides of calcium and sodium are solid and crumble away or dissolve. Thus the glass is completely disintegrated. The vapor of hydrofluoric acid, generated in the way described above from calcium fluoride in a lead dish, is used for etching glass. The surface of the glass is covered with paraffin to protect it from the action of the vapor, and with a sharp instrument portions of this paraffin are removed where the etching effect is desired. The vapor gives a rough surface where it encounters the glass (**test** for a fluoride). Burettes and other glass-ware are graduated in this fashion. The aqueous solution, which may also be employed, makes smooth depressions on the surface. The aqueous solution of the acid is **used** in the analysis of minerals containing silicates, which frequently are not attacked by other acids. It is used also for removing sand from metal castings and for cleaning the exteriors of buildings of granite and sandstone.

The Halogens as a Family

The reader is recommended to compare carefully the properties of the several halogens and their compounds with hydrogen. It will be found that, while very striking similarities exist throughout the whole halogen family in the case of nearly every physical and chemical property, there is always a regular gradation in properties in the order of the atomic weights, namely F, Cl, Br, I. A few examples are noted below; the student should tabulate the rest himself for his own convenience.

Color in liquid state: F_2 yellow; Cl_2 greenish-yellow; Br_2 brown; I_2 deep violet.
Boiling-point: F_2 —187°; Cl_2 —34°; Br_2 59°; I_2 184°.
Action on hydrogen: F_2 very rapid action in cold, without light;

Cl_2 action rapid in cold, only with strong light; Br_2 action rapid only when heated; I_2 action slow and incomplete even when heated.

Heat of Formation of Potassium Salt: $\frac{1}{2}K_2F_2$, 118,100 cals.; KCl, 104,300 cals.; KBr, 95,100 cals.; KI, 80,100 cals.

As an aid to the memory, such a table is exceedingly valuable. But it is really not necessary to attempt to memorize *all the properties* of each halogen and of each halogen compound *separately*. The properties of bromine, for example, are all intermediate between those of chlorine and iodine. Indeed, when bromine was first examined by Liebig, he thought it was an unstable compound of chlorine and iodine, and so missed gaining the credit of its discovery as an element.*

The *activity* of the halogens, as is evident from their action on hydrogen and on metals (see potassium above), decreases in the order of increasing atomic weight. This is seen also in their displacement reactions in solutions. Thus we have found that chlorine displaces bromine from bromides and that bromine displaces iodine from iodides. Fluorine is able to displace even chlorine from chlorides: $2Cl^- + F_2 \rightarrow 2F^- + Cl_2$. When we note also that the halogens displace sulphur from sulphides (compare p. 353) and that oxygen displaces iodine from hydriodic acid, we are able to draw up an **order of activity for the non-metals,** similar to the activity order for the metals. This order of activity expresses the order of preference of the non-metals for assuming the ionic state, or for gaining electrons (compare p. 313). Starting from the top, it is F, Cl, Br, O, I, S.

A last point worthy of mention is that some of the properties of fluorides are peculiar. Thus hydrogen fluoride at low temperatures has the formula H_2F_2, and its solution in water is not very highly ionized. We shall see later that it is usual for the first member of a family of elements or compounds to exhibit a few peculiarities. In fact we have already noted, at the beginning of this chapter, one peculiarity of the first of all the elements, hydrogen. Although a non-metal, it gives a *positive* ion H^+.

* Iodine unites with chlorine to form two compounds. The most familiar is a red crystalline substance **iodine monochloride** ICl. The **trichloride** ICl_3 is made by the use of excess of chlorine. Iodine unites with bromine to form the compound IBr, while a compound with fluorine IF_5 is supposed to exist. None of these compounds is particularly stable, and some of them decompose very easily.

Exercises. — 1. Tabulate the properties of fluorine, chlorine, bromine, and iodine, and of their compounds with hydrogen.

2. How should you distinguish by chemical reactions the chloride, bromide, iodide, and fluoride, (*a*) of hydrogen, (*b*) of sodium, from one another?

3. Write equations for the action, (*a*) of chlorine upon a solution of hydrogen sulphide, (*b*) of bromine upon a solution of hydrogen iodide, (*c*) of oxygen upon a solution of hydrogen iodide, (*d*) of fluorine upon a solution of hydrogen iodide.

4. Why does hydriodic acid, when left in the air, become brown in color?

5. Make a list of all the acids we have encountered, and note which are weak and which strong.

6. How should you make potassium bromide, starting with, (*a*) potassium and bromine, (*b*) hydrogen bromide, (*c*) potassium iodide?

7. Rewrite the equation for the action of hydrobromic acid on silver nitrate solution in full ionic form.

8. At a given temperature, would increasing the pressure in a mixture of hydrogen and bromine vapor render the union more or less complete? Is the union more complete at a high or at a low temperature?

9. What volume of chlorine at 10° and 750 mm. will be required to displace all the bromine from 100 c.c. of a 0.5 N solution of sodium bromide?

10. What volume of chlorine at 10° and 750 mm. will be required to displace all the iodine from 100 c.c. of a 0.5 N solution of potassium iodide?

11. What volume of HBr gas at 20° and 745 mm. will be obtained by cautious addition of water to 10 g. of phosphorus tribromide (p. 346)?

12. What weight of iodine is contained in 1 metric ton of crude Chile saltpeter, analyzing 0.2 per cent $NaIO_3$?

13. A 10 liter cylinder, full of dry hydrogen iodide and covered with a glass plate, is brought mouth to mouth with a 5 liter cylinder full of chlorine. What do you observe when the plate is removed? Explain.

14. If the above experiment is done twice, (*a*) with the cylinder of chlorine uppermost, (*b*) with the cylinder of hydrogen iodide uppermost, what differences do you observe? Discuss fully.

15. Devise a method, based upon the law of freezing-point depression (p. 216), to prove that iodine added to concentrated KI solution is not in a state of physical solution, but is combined with the potassium iodide (p. 350).

16. A tube at 283° contains an equilibrium mixture of hydrogen iodide and its dissociation products (p. 352). Devise methods of forcing the reversible reaction to completion, (*a*) in the forward direction, (*b*) in the backward direction, without changing the temperature.

17. The density of constant boiling-point hydriodic acid at 15° is 1.680. It contains 57.0 per cent of hydrogen iodide by weight. What is its weight-normality (p. 202)? What is its volume-normality?

18. What is the percentage composition of iodoform CHI_3?

19. What kind of a salt is potassium-hydrogen fluoride? How would it dissociate in aqueous solution? Approximately how many times the normal freezing-point depression would 1 g. mol. wt. of the salt dissolved in 1000 g. of water give? Justify your answer (pp. 317–8).

20. What is the percentage composition of cryolite (p. 355)?

21. Is the following statement correct: "Hydrofluoric acid is a very strong acid, *because it eats glass*"? Discuss briefly (p. 318).

22. Is hydrogen fluoride below 40° (p. 356) lighter or heavier than hydrogen chloride? What is the vapor density of silicon tetrafluoride referred to air?

23. If you had been in Liebig's place (p. 359), how would you have proceeded in order to prove that the substance that you had under examination was *not* an unstable compound of chlorine and iodine?

24. Show that the following data for the distribution of iodine between water and carbon disulphide are in conformity with the law of partition (p. 220). Plot concentration in water layer against concentration in carbon disulphide layer, and calculate the relative solubility of iodine in equal volumes of the two solvents.

G. iodine in 100 c.c. of water layer	0.044	0.032	0.016	0.010
G. iodine in 100 c.c. of CS_2 layer	17.4	12.9	6.6	4.1

25. What exceptional points in the behavior of fluorine compounds, as compared with corresponding compounds of the other halogens, can you discover from an examination of the solubility tables on the inside front cover?

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CHAPTER XXI

OXIDIZING SUBSTANCES

In the preceding chapters we have encountered several rather confusing *oxidizing reactions*. For example, in the preparation of chlorine by the action of $KMnO_4$ on HCl (p. 239), it was stated that the hydrogen chloride was oxidized to chlorine and the potassium permanganate reduced to manganous chloride. The student may have found it difficult to understand how we can regard a substance as oxidized when no oxygen is added to it. In order to explain oxidations more clearly, particularly in connection with the conception of valence, we must now learn more about oxidation in general. We can do this best through the study of three oxidizing substances which are of a simpler nature and are all in common use. These are **ozone, hydrogen peroxide,** and **hypochlorous acid.**

Ozone O_3

A fresh, penetrating odor, resembling that of very dilute chlorine, was noticed by van Marum (1785) near an electrical machine in operation. Schönbein (1840) showed that the odor was that of a distinct substance, which he named ozone (Greek, *to smell*), and he discovered a number of ways of obtaining it. It is very questionable whether there is any ozone in the air, excepting temporarily in the immediate neighborhood of a natural or artificial discharge of electricity.

Preparation of Ozone. — The most satisfactory way of preparing ozone is to pass a silent electrical discharge through oxygen. The original ozonizer of Siemens (Fig. 117) consists of two co-axial glass tubes, between which the oxygen flows. The discharge is produced by connecting an outer layer of tinfoil on the outer tube, and an inner layer of tinfoil in the inner tube, with the poles of an induction coil. With an improved modern apparatus and dry, cold oxygen, as much as 20 per cent of the gas may be converted into ozone.

Traces of ozone are found in the oxygen generated by electrolysis of dilute sulphuric acid (p. 134), or by the action of concentrated sulphuric acid on barium peroxide. It arises also during the slow oxidation of phosphorus by the air. Significant quantities are obtained when oxygen (or air) is exposed to ultra-

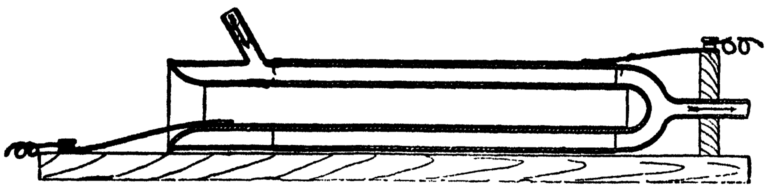


FIG. 117. Preparation of Ozone.

violet light. Ozone is formed also when a jet of burning hydrogen, or an electrically-heated loop of platinum wire, is immersed in liquid oxygen. This method shows that ozone is formed at high temperatures, and survives when cooled suddenly by the liquid oxygen.

A convenient way of demonstrating its formation by heating is to immerse a platinum wire, heated white hot by an electric current, or a small jet of burning hydrogen, under the surface of some liquid air. The ozone is formed close to the hot wire or flame, and is instantly cooled as it leaves that region by contact with the liquid air (—190°), and so 1.5–2 per cent of it is found in the gases evaporated by the heat. A recognizable trace of ozone is even formed when a small jet of oxygen is blown through the tip of a Bunsen flame.

Physical Properties of Ozone. — Ozone is a gas of blue color. It boils at —112°, so that when a mixture of oxygen and ozone is led through a **U**-tube immersed in liquid oxygen (—182.5°), the ozone collects in the tube as a deep-blue fluid. Ozone is much more soluble in water than is oxygen. At 12°, 100 volumes of water would dissolve 50 volumes of the gas at one atmosphere pressure.

It has been claimed that, when liquid ozone is distilled, the last portion contains **oxozone** O_4 (C. Harries), but the evidence regarding the existence of this substance is still inconclusive.

Chemical Properties of Ozone. — The density of ozone is one-half greater than that of oxygen. Its molecular weight is therefore 48, and its formula O_3. Being formed with absorption of energy, ozone is most stable at very high temperatures (Van't Hoff's law, p. 284):

$$3O_2 + 61{,}400 \text{ cal.} \rightleftarrows 2O_3.$$

When produced in cold oxygen, by use of electrical energy, it decomposes slowly. The attainment of equilibrium in this case, like all others, is hastened by raising the temperature. Equilibrium is reached practically instantly at 250–300°, and at these temperatures decomposition is still practically complete. Liquid ozone sometimes decomposes explosively. As the equation shows, two volumes of ozone give three of oxygen.

Ozone can be kept undecomposed only when mixed with much oxygen. Hence its density and molar weight cannot be ascertained save by indirect means. The method of attack may be most readily understood by the student by solving the following problem.

A sample of ozonized oxygen is divided into two parts. The first is bubbled through turpentine, previously saturated with ordinary oxygen. All of the ozone is thereby removed, by absorption, to form stable "ozonides," and the volume of the gas is found to be reduced from 1000 c.c. to 950 c.c. The second part is heated to 250°, and brought back to its original temperature. Its volume is found to be increased from 1000 c.c. to 1025 c.c. Calculate from these data the molecular weight of ozone.

Ozone is a much more active oxidizing agent than oxygen. Mercury and silver, which are not affected by the latter, are converted into oxides by the former. Silver gives the peroxide, Ag_2O_2, thus:

$$2Ag + 2O_3 \rightarrow Ag_2O_2 + 2O_2.$$

Paper dipped in starch emulsion containing a little potassium iodide is used as a **test** for ozone:

$$O_3 + 2KI + H_2O \rightarrow O_2 + 2KOH + I_2.$$

The iodine gives a deep-blue color to the starch (see p. 350). This test, however, will not distinguish ozone from chlorine or hydrogen peroxide, and may, therefore, be used only in the absence of these substances.

Ozone may be distinguished from chlorine, nitrogen tetroxide, and other oxidizing agents, with the exception of hydrogen peroxide, by using pink litmus paper instead of plain paper to carry the potassium iodide solution in the above test. The potassium hydroxide set free by ozone turns the paper blue. Chlorine, for example, gives an entirely different action: $Cl_2 + 2KI \rightarrow 2KCl + I_2$.

Ozone also removes the color from many of the vegetable coloring matters and artificial dyes. It should be understood that the great majority of the complex compounds of carbon are colorless. Even

a slight chemical change, affecting only one or two of the atoms in a complex molecule, is thus almost sure to give a colorless or much less strongly colored material. **Indigo,** $C_{16}H_{10}N_2O_2$, which has a deep-blue color, is an example of a vegetable dye that is also made artificially. When ozonized air is bubbled through a dilute solution of this dye (as indigo-carmine), the indigo is oxidized to isatin $C_8H_5NO_2$, and the color disappears (see below).

Ozone is used commercially in bleaching oils, waxes, ivory, flour, and starch. It is employed also for purifying air in underground railways and for sterilizing drinking water in Paris, Leningrad, and other cities. For this latter purpose, however, bleaching powder is, in general, less expensive.

Allotropic Modifications. — We have seen (p. 163) that a substance may exist in more than the three regular states, solid, liquid, and gaseous. When a substance shows more than one form, in the same state, like oxygen and ozone, we call them **allotropic modifications** (compare p. 399).

Strictly speaking, of course, oxygen and ozone are *different* substances (p. 6), since they have different properties. The difference in density, interpreted in terms of the molecular hypothesis, gives us one statement of the nature of the difference, which is embodied in the formulæ O_2 and O_3. The difference in activity, interpreted in terms of the conception of energy, gives us another method of stating the nature of the difference. The recent preference for the second method is well illustrated by this case. The first method uses a mere physical property, the second a fact which is intimately connected with the whole *chemical behavior* of the substance, a matter of much greater interest to the chemist.

Oxidizing Agents, and Explanation of Their Activity. — When ozone turns into oxygen much heat is liberated (equation, p. 363). Ozone possesses, therefore, much more internal energy than does oxygen. On this account it brings to the task of oxidizing any substance more energy than does oxygen itself, and is therefore more efficient. Thus, free oxygen does not interact in the cold with indigo, or with silver or potassium iodide, while ozone oxidizes them rapidly.

The reason for this difference is shown more clearly by means of thermochemical equations (p. 260). When one gram-molecular weight of indigo is oxidized by ozone to isatin, 63,200 calories of heat are liberated:

$$C_{16}H_{10}N_2O_2 + 2O_3 \rightarrow 2C_8H_5NO_2 + 2O_2 + 63{,}200 \text{ calories.} \quad (1)$$

But we have seen above that the same quantity of ozone, decomposing into oxygen, liberates 61,400 calories of heat:

$$2O_3 \rightarrow 3O_2 + 61{,}400 \text{ calories.} \qquad (2)$$

Now it is a characteristic of thermochemical reactions that, when they are added or subtracted, the heat effect of the resultant reaction is equal to the sum or difference of those of the original reactions (p. 262). Thus, whether we burn carbon (p. 95) directly to carbon dioxide CO_2, or whether we burn it first to carbon monoxide CO and then burn this to CO_2, exactly the same amount of heat is evolved:

$$\begin{array}{l} 2C + O_2 \rightarrow 2CO + 58{,}000 \text{ calories} \\ 2CO + O_2 \rightarrow 2CO_2 + 135{,}800 \text{ calories} \\ \hline 2C + 2O_2 \rightarrow 2CO_2 + 193{,}800 \text{ calories} \end{array}$$

Employing this principle, we can discover what would be the amount of heat liberated if indigo could be oxidized to isatin by oxygen gas, by subtracting equation (2) from equation (1) above, even although the reaction so represented cannot be conveniently carried out. The result is:

$$C_{16}H_{10}N_2O_2 + O_2 \rightarrow 2C_8H_5NO_2 + 1{,}800 \text{ calories} \qquad (3)$$

The heat liberated in equation (1) is consequently 35 times as great as in equation (3). In view of what has been said in a previous chapter (p. 259) regarding the speed of a chemical change, and the quantity of energy available because of it, the greater efficiency of ozone as an oxidizing agent will now be readily understood.

It should be noted that when ozone acts as an oxidizing agent, usually only one of the atoms of oxygen in each molecule plays this part, and oxygen gas is formed. This is illustrated in all the three equations cited in the preceding sections.

Hydrogen Peroxide H_2O_2

Hydrogen peroxide is found in minute amounts in rain and snow. It is formed in small quantities, in a way not at present fully understood, when moist metals, like zinc, lead, and copper, rust.

When a hydrogen flame is allowed to play upon ice, appreciable amounts of the peroxide are saved from being decomposed, as they ordinarily would be by

the heat of the action, and are found in the water. It is formed also to the extent of 37 per cent when a silent electrical discharge passes through a mixture of hydrogen and oxygen cooled by liquid air (—190°). It is produced when oxygen is passed, close to the negative electrode, through the liquid in an electrolytic cell containing dilute sulphuric acid. The gas is reduced by the hydrogen being liberated on the platinum plate.

Preparation. — Sodium peroxide Na_2O_2, produced by burning sodium in dry air, can be dissolved, a little at a time, in *ice-cold* water without much evolution of oxygen (contrast p. 93). When this solution is acidified with hydrochloric or sulphuric acid, a double decomposition takes place:

$$Na_2O_2 + 2HCl \rightleftarrows 2NaCl + H_2O_2$$

and a dilute solution of hydrogen peroxide (mixed with common salt) is obtained. The fact that the reaction proceeds practically to completion in the forward direction shows (see p. 334) the product to be a very weak acid, with the negative radical O_2^{II}.

For manufacturing purposes it is more convenient to use barium peroxide BaO_2, suspended in water, and sulphuric acid:

$$BaO_2 + H_2SO_4 \rightarrow BaSO_4 \downarrow + H_2O_2$$

because the precipitation of insoluble barium sulphate carries the reaction to completion. The precipitate is filtered off and a clear solution of hydrogen peroxide obtained.

An aqueous solution is also obtained by passing carbon dioxide through barium peroxide suspended in water:

$$BaO_2 + CO_2 + H_2O \leftrightarrows BaCO_3 \downarrow + H_2O_2.$$

Pure hydrogen peroxide is isolated from any of these solutions by distillation under reduced pressure. To secure the low pressure, the ordinary distilling apparatus (Fig. 11, p. 30) is made completely airtight, and is connected by a branch tube with a water-pump. Hydrogen peroxide is much less volatile than water, but decomposes into water and oxygen violently at 100°. Hence the lower pressure is required to make possible its volatilization at a temperature below this point. At 26 mm. pressure, the water begins to pass off first (at about 27°). The last portion of the liquid boils at 69° and is hydrogen peroxide.

By evaporating the commercial (3 per cent) solution at 70°, a liquid containing 45 per cent of hydrogen peroxide may be made without much loss of the material by volatilization.

Most of the hydrogen peroxide now manufactured is obtained by electrolytic processes (see p. 433).

Physical Properties. — Hydrogen peroxide (100%) is a syrupy liquid of sp. gr. 1.5. It blisters the skin and, when diluted, has a disagreeable metallic taste. The pure substance freezes at — 1.7°.

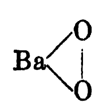
Chemical Properties. — Hydrogen peroxide (100%) is very **unstable,** and decomposes slowly even at low temperatures. The dilute aqueous solution, when free from impurities, keeps fairly well. The presence of a trace of free acid or of certain organic substances, such as acetanilide, increases its stability (see p. 104). Free alkalies and most salts assist the decomposition; hence the necessity for purifying the commercial solution. Addition of powdered metals, of manganese dioxide, or of charcoal (*contact action*) causes effervescence even in dilute solutions, and oxygen escapes:

$$2H_2O_2 \rightarrow 2H_2O + O_2.$$

Since the substance cannot be vaporized, even at low pressure, without some decomposition, its molecular weight has been determined by the freezing-point method. It has been found that a solution containing 31.8 g. of the substance in 1000 g. of water freezes at — 1.86°. Hence, by reference to p. 217, we obtain 31.8 as the approximate molecular weight. Now the formula HO corresponds to a molecular weight of 17 and H_2O_2 to one of 34. It is evident, therefore, that the latter is the correct formula.

Hydrogen peroxide, in solution in water, is a very **feeble acid.** As such it enters into double decompositions readily, and the peroxides are salts with the negative radical O_2^{II}. The bivalent character of the radical O_2 may be more clearly expressed by the following graphic formulæ for hydrogen peroxide and its most familiar salt, barium peroxide:

$$H—O—O—H$$



We have seen (p. 367) that when acids act upon barium peroxide BaO_2, hydrogen peroxide is formed: $BaO_2 + H_2SO_4 \rightarrow BaSO_4 + H_2O_2$. But all oxides containing two atoms of oxygen in each molecule do not yield hydrogen peroxide. Thus, lead dioxide PbO_2, and manganese dioxide MnO_2, when treated with sulphuric acid, give the sulphate of the metal and water and oxygen:

$2MnO_2 + 2H_2SO_4 \rightarrow 2MnSO_4 + 2H_2O + O_2$. We infer from this that the two sets of dioxides are not alike. With barium peroxide there is a simple double decomposition, or exchange of radicals, and so we hold that it contains the radical O_2 which is bivalent as a whole: $Ba^{II}(O_2)^{II}$. This harmonizes with the fact that no other compound is known in which barium has even the appearance of being quadrivalent. Manganese dioxide can give a tetrachloride (p. 240), however, as can also lead dioxide (p. 832), so we infer that the manganese and lead are here quadrivalent. The graphic formulæ for these two substances may be written $O = Mn = O$ and $O = Pb = O$ respectively. On comparing these formulæ with those for hydrogen peroxide and barium peroxide given above, the difference in constitution becomes obvious.

If it were merely a question of composition, the substances should behave alike. So, also, we often have two or more compounds identical in molecular weight, and in the elements and numbers of units which they contain, which are nevertheless totally different in physical and chemical properties. To account for this difference we often find it convenient to suppose (and frequently we are able to confirm our assumption) that, although the atoms contained in the two or more kinds of molecules are of the same numbers and kinds, **the atoms are in different geometrical arrangement towards one another.** Sometimes one of these substances can be made directly from the other, and this gives us that variety of chemical change which was named internal rearrangement (p. 232). Thus, ammonium cyanate NH_4NCO, when heated in aqueous solution, turns into urea $CO(NH_2)_2$, a substance with totally different chemical properties.

Hydrogen peroxide is a much more active **oxidizing agent** than is free oxygen. This would be expected from the fact that it contains so much more internal energy than the water and oxygen into which it decomposes, that 23,100 calories are evolved in the decomposition of one gram-molecular weight. Thus, it liberates iodine from hydrogen iodide:

$$2HI + H_2O_2 \rightarrow 2H_2O + I_2.$$

It converts sulphides into sulphates. The white lead (see p. 833) used in paintings is changed by the hydrogen sulphide in the air of cities to black lead sulphide: $Pb_3(OH)_2(CO_3)_2 + 3H_2S \rightarrow 3PbS + 4H_2O + 2CO_2$. This may be oxidized to white lead sulphate by means of hydrogen peroxide:

$$PbS + 4H_2O_2 \rightarrow PbSO_4 + 4H_2O,$$

and in this way the original tints of the picture may be practically restored. Caution must be exercised in carrying out the process, however, since many organic coloring matters are also changed by hydrogen peroxide into colorless substances by an action similar to that of ozone (see p. 365). Hence hydrogen peroxide is used for

bleaching silk, feathers, hair, and ivory, which would be destroyed by a more violent agent. The products of its decomposition, being water and oxygen only, are harmless and, on this account, it is used in disinfecting (destroying organisms in) sores, and as a throat wash.

Hydrogen peroxide exercises the functions of a **reducing agent** in special cases, also. Thus, silver oxide is reduced by it to silver:

$$Ag_2O + H_2O_2 \rightarrow 2Ag + H_2O + O_2.$$

A solution of potassium permanganate, to which sulphuric acid has been added, is also rapidly reduced to manganous sulphate:

$$2KMnO_4 + 3H_2SO_4 + 5H_2O_2 \rightarrow 2MnSO_4 + K_2SO_4 + 8H_2O + 5O_2.$$

The above action is used in quantitative analysis for estimating the quantity of hydrogen peroxide in a given liquid after the liquid has been acidified. The amount of a standard solution of the permanganate which is required to decompose all the peroxide is measured by means of a burette (p. 336). The permanganate is deep reddish-purple in color, while the products are colorless. Hence after the peroxide is exhausted, the next drop of the permanganate confers a distinct, permanent, pink tinge upon the liquid. The addition of the permanganate solution is stopped so soon as this condition is reached and the volume of it that has been used is read off.

The following reaction is used as a *test* for hydrogen peroxide. When a solution of potassium dichromate $K_2Cr_2O_7$ is acidified with sulphuric acid and a drop of the mixture is added to aqueous hydrogen peroxide, an unstable substance possessing a deep, brilliant blue color is formed. The test is rendered more delicate by shaking with a few drops of ether, since the blue compound is more soluble, and also more stable, in this liquid than in water. By this test the presence of hydrogen peroxide in rain water can often be demonstrated.

Hypochlorous Acid HOCl

Of the many compounds of chlorine which contain oxygen, *two* have already been mentioned — potassium chlorate $KClO_3$ (p. 91) and hypochlorous acid HOCl (p. 245). We shall here take up the latter of these as a third example of an oxidizing agent, and shall then devote the next chapter to a systematic discussion of the oxygen compounds of the halogens.

Pure Hypochlorous Acid. — A pure solution of the acid may be made by dissolving chlorine monoxide Cl_2O in water. **Chlorine monoxide** is a brownish-yellow, explosive gas (b.-p. 5°), made by

passing chlorine gas over warmed mercuric oxide * HgO (Fig. 17, p. 44). Each of the constituents of the oxide combines with chlorine:

$$HgO + 2Cl_2 \rightarrow HgCl_2 + Cl_2O.$$

The mercuric chloride then unites with another formula-weight of the mercuric oxide to form a solid basic mercuric chloride HgO, $HgCl_2$, which remains in the tube. Both the gaseous and liquefied forms of chlorine monoxide, the former when warmed, the latter when touched by paper or dust, decompose into its constituents with explosion. The gas dissolves in water very easily (200 : 1, by vol.). The yellow solution of hypochlorous acid which results:

$$Cl_2O + H_2O \leftrightarrows 2HOCl,$$

has a strong odor of chlorine monoxide, because the combination is reversible, as it is in sulphurous acid (p. 415).

As *an acid,* hypochlorous acid is very weak, being very little decomposed into its ions, H^+ and $(OCl)^-$. With bases, it gives **hypochlorites** (see p. 374).

A concentrated solution tends to lose chlorine monoxide, as we have already noted. A second change which gradually takes place in a concentrated solution is a "self-oxidation" of part of the acid by another part to **chloric acid** $HClO_3$:

$$3HOCl \rightarrow HClO_3 + 2HCl.$$

It is *unstable in still another direction* even in dilute solution, exposure to sunlight being sufficient to cause it to give up oxygen, which rises in bubbles through the solution:

$$2HOCl \rightarrow 2HCl + O_2 \uparrow.$$

Heat is given out in the action, and the stable hydrochloric acid remains.

It is a most *active oxidizing agent* because of this tendency to give up oxygen with liberation of energy. Thus, its solution oxidizes organic colored substances, producing colorless or less strongly colored ones:

$$\underset{\text{indigo}}{C_{16}H_{10}N_2O_2} + 2HOCl \rightarrow \underset{\text{isatin}}{2C_8H_5NO_2} + 2HCl.$$

* The crystalline, red oxide is not sufficiently active. The oxide must be precipitated from sodium hydroxide and mercuric nitrate solutions, it must be thoroughly washed on a filter, and dried at 300–400° before use.

Used as a disinfectant (see p. 375), it oxidizes and destroys bacteria. Hypochlorous acid is *more energetic* as an oxidizing agent than is ozone or hydrogen peroxide, and is used extensively in *bleaching*.

Chlorine-Water. — It will be recalled that chlorine acts chemically upon water (p. 245):

$$Cl_2 + H_2O \rightleftharpoons HCl + HOCl.$$

giving hydrochloric acid and hypochlorous acid. The action is reversible, and in half-saturated chlorine solution (freshly made and protected against bright sunlight, see above) about one-third only of the chlorine has undergone the change shown in the equation. But, if a substance which can be oxidized, such as a dye (attached, perhaps, to cloth), is introduced into the solution, the HOCl which is present transfers its oxygen to the dyestuff. This leaves HCl *alone* in the solution, and stops the backward reaction. Hence more of the chlorine acts upon the water, and more hypochlorous acid is formed. This, in turn, is used up. Thus, in a few moments, all the free chlorine is gone, only dilute hydrochloric acid remains, and a colorless organic compound is left on the cloth or in the solution.

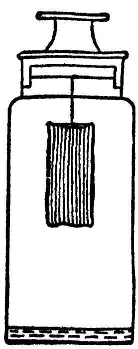


FIG. 118. Experiment to Demonstrate That Dry Chlorine Is Not a Bleaching Agent.

Chlorine itself is often, erroneously, spoken of as the bleaching agent. If a *dry*, colored cloth be hung for a week in chlorine, dried by having sulphuric acid in the bottle (Fig. 118), little or no change in color will occur. But a *wet* rag is bleached as soon as the chlorine has time to dissolve in the water and give the necessary hypochlorous acid.

Flowers are bleached by dry chlorine gas, because by their nature they contain the indispensable water.

Thermochemistry of Hypochlorous Acid. — As we have seen (p. 258), chemical changes which proceed spontaneously are accompanied by a transformation of free internal energy into some other form of energy. Hence, a substance, or system of substances, which undergoes such a change, possesses more chemical energy and activity before the change than after it. In consequence, if some given chemical change *uses* the products of such an action, and can be

brought about by the employment of the original substance, the employment of the latter will involve a greater liberation of energy, and will therefore be more likely to secure the consummation of the change in question.

The decomposition of hypochlorous acid and of chlorine monoxide are cases where there is a very marked difference between the amount of chemical energy in the original substances and in the products of decomposition, hydrogen chloride and free oxygen in the first case, and free chlorine and oxygen in the second. Hence the changes into these substances sometimes are of the nature described as explosive. A more important fact, however, is that, on this account, hypochlorous acid and chlorine monoxide are more active oxidizing agents than is free oxygen gas. The energy liberated in the decomposition of the hypochlorous acid has to be *added* (p. 262) to that which free oxygen could give, if performing the same oxidation, in order that **the total fall in energy,** which **measures the tendency of the action to take place,** may be estimated. Hence, substances that are not affected by free oxygen may be changed instantly by hypochlorous acid. This explains, for example, the oxidation by hypochlorous acid of many carbon compounds, including those which are colored, when atmospheric air is without action. Thus, the heat liberated in the oxidation of indigo to isatin by oxygen gas, if it could be carried out, would be 1800 cal. (p. 366). The much greater heat liberated when hypochlorous acid is used, we obtain by adding the thermochemical equations:

$$2HOCl \rightarrow 2HCl + O_2 + 18{,}600 \text{ cal.}$$
$$C_{16}H_{10}N_2O_2 + O_2 \rightarrow 2C_8H_5NO_2 + 1800 \text{ cal.}$$
$$\overline{C_{16}H_{10}N_2O_2 + 2HOCl \rightarrow 2C_8H_5NO_2 + 2HCl + 20{,}400 \text{ cal.}}$$

Formerly a different explanation for actions like that of hypochlorous acid, when it behaves as an oxidizing agent, was offered. It was suggested that the oxygen was first liberated from the acid: $HOCl \rightarrow HCl + O$, and that the single *atoms* of the element so produced were more active than molecular oxygen. Exactly how the hypochlorous acid, lacking all consciousness, knew that an oxidizable body was present, and proceeded to liberate the atoms of oxygen, was never explained. This oxygen, which was supposed to interact in the moment of its production, was called **nascent oxygen.** But it will be seen that such an explanation is entirely unnecessary. The activity of the hypochlorous acid on account of its large store of free energy sufficiently accounts for the facts (see also p. 246).

Preparation of Hypochlorites. — For industrial purposes, pure hypochlorites are not, as a rule, required. Hence, commercial

sodium or **potassium hypochlorite** is prepared by the action of sodium or potassium hydroxide on chlorine-water. The latter contains both hydrochloric and hypochlorous acids, and so a solution containing a mixture of sodium or potassium chloride and hypochlorite is obtained:

$$Cl_2 + H_2O \rightleftarrows HCl + HOCl. \quad (1)$$
$$HCl + KOH \rightarrow KCl + H_2O. \quad (2)$$
$$HOCl + KOH \rightarrow KOCl + H_2O. \quad (3)$$

Although action (1) is only partial, being strongly reversible, the neutralization of the two acids in actions (2) and (3) displaces the first equilibrium, and all three actions proceed to completion. Omitting the substances which appear on both sides, we get, by addition of the three equations (compare p. 366), the final equation:

$$Cl_2 + 2KOH \rightarrow KCl + KOCl + H_2O.$$

When a solution of sodium chloride is electrolyzed, sodium hydroxide and chlorine are produced at the opposite electrodes (p. 234). Ordinarily, care is taken to keep these two substances separate, but sodium hypochlorite may be readily obtained if no diaphragm is used and the solution is well stirred during the electrolysis. Several types of hypochlorite cells are now in extensive use.

Bleaching Powder. — The "bleaching powder" used in industry is commonly made by the action of chlorine on slaked lime. This action is usually written:

$$Ca(OH)_2 + Cl_2 \rightarrow CaCl(OCl) + H_2O,$$

but recently X-ray analysis (see p. 64) has shown that the solid material is essentially a mixture of calcium hypochlorite $Ca(OCl)_2$ and the basic chloride $CaCl_2,Ca(OH)_2,H_2O$.

In solution it gives the ions Ca^{++}, Cl^-, and $(OCl)^-$. In other words, a solution of bleaching powder in water acts like mixed solutions of calcium chloride and calcium hypochlorite. Only the calcium hypochlorite is concerned in the bleaching process. When the solution is exposed to the air, it gradually absorbs carbon dioxide (see p. 457). This dissolves in the solution to form carbonic acid H_2CO_3, which by double decomposition liberates hypochlorous acid:

$$Ca(OCl)_2 + H_2CO_3 \rightleftarrows CaCO_3 + 2HOCl.$$

If now materials which it is desired to bleach by oxidation are introduced into the solution, the HOCl is used up, stopping the backward reaction and carrying the decomposition finally to completion.

Bleaching. — Cotton and linen, in their original states, are not pure white. Bleaching is therefore an extensive and most important industry. The yarn or cloth must first be freed from cotton-wax and tannin, since the former would hinder the action of the bleaching agent, and both would also make the subsequent dyeing uneven. The material is therefore first boiled with dilute caustic soda solution, and washed with water. The goods are then first "chemicked" in cold bleaching powder solution; next "soured" by immersion in *very dilute* sulphuric or hydrochloric acid; and finally washed with extreme thoroughness.

The final *washing*, to remove all traces of chlorine and bleaching powder, is absolutely necessary. If not removed, the hypochlorous acid acts gradually upon the cotton or linen and "rots" it. Bleaching agents, when used in the household, carelessly, are liable to cause extensive damage for this reason. A dilute solution of sodium thiosulphate (photographer's "hypo") is often used, as "anti-chlor," to interact with and remove the last traces of chlorine.

Cotton and linen are composed of cellulose $(C_6H_{10}O_5)_y$, a rather inert substance, and one which is very slowly acted upon by dilute hypochlorous acid. Hence, with brief contact and proper handling, no damage is done. Wool, silk, and feathers, however, are composed largely of compounds (proteins) containing nitrogen (up to 15 per cent) in addition to the above three elements. Their constituent material interacts as easily with hypochlorous acid as do the traces of coloring substances. Hence, since the fabric itself would be attacked by this agent, hydrogen peroxide or sulphurous acid (p. 417) is used for bleaching these materials.

Bleaching Powder as a Disinfectant. — A disinfectant is a substance which destroys bacteria and other minute, and often harmful, organisms. Bleaching powder has a distinct odor, due to the slow action of the carbon dioxide and moisture of the air upon the salt, liberating hypochlorous acid. Bleaching powder, when scattered around, will therefore *disinfect* the surrounding air, because the hypochlorous acid thus liberated kills by *oxidation* all bacteria present.

When an epidemic of typhoid fever occurs, it is usually traced to the presence of colon bacilli and typhoid organisms in the *drinking water*. The most effective means of destroying these bacilli is to add, at the distributing point, a small proportion of bleaching powder (about 20 pounds per million gallons of water).

Recently, *chlorine-water* has in many cases taken the place of bleaching powder for this purpose. Cylinders of liquid chlorine (p. 242) were used in the World War much more extensively for

germicidal than for poison gas purposes, all water supplies being sterilized, whenever possible, by the addition of very minute amounts of chlorine. One of the best antiseptics used on wounds during the World War was Carrel-Dakin solution, which is prepared by passing chlorine into a solution of sodium carbonate (washing soda).

Oxidation and Reduction

Oxidations Previously Mentioned. — The simplest oxidations are reactions in which free oxygen is actually used up, for example in the *union of oxygen* with metals and with non-metals:

$$2Cu + O_2 \rightarrow 2CuO.$$
$$S + O_2 \rightarrow SO_2.$$

The displacement of another element from a compound by oxygen is also oxidation:

$$4HCl + O_2 \rightleftarrows 2H_2O + 2Cl_2.$$

The transfer of combined oxygen from one substance to another in a reaction is again oxidation:

$$2KMnO_4 + 16HCl \rightarrow 8H_2O + 2KCl + 2MnCl_2 + 5Cl_2.$$
$$MnO_2 + 4HCl \rightarrow MnCl_2 + Cl_2 + 2H_2O.$$

What is the substance oxidized in the last three reactions? It is *hydrochloric acid,* and the product of its oxidation is *chlorine.* True, we have added no oxygen to chlorine itself in any of these reactions, but we have done something which is exactly equivalent to addition of oxygen, we have *taken away hydrogen,* and we have not replaced that hydrogen by any other positive element.

Note that *every oxidation is accompanied by reduction of the oxidizing agent.* Thus, in the first of the three reactions just discussed, the free oxygen is reduced to water. In the other reactions, $KMnO_4$ and MnO_2 are reduced to $MnCl_2$. In all three cases HCl is the *reducing agent.*

Other Cases of Oxidation. — But oxygen is only one of a class of elements which we call non-metallic or negative elements, so that we do not *restrict* the term "oxidation" to actions involving oxygen. Thus, forming a sulphide, by heating a metal with sulphur, is oxidation also:

$$Fe + S \rightarrow FeS.$$

Similarly, changing ferrous chloride $FeCl_2$ to ferric chloride $FeCl_3$ is oxidation:

$$2FeCl_2 + Cl_2 \rightarrow 2FeCl_3.$$

In every polar compound one of the elements is relatively positive and the other relatively negative. Here, iron is positive, sulphur and chlorine are negative.

Oxidation, then, is **introducing or increasing the proportion of the negative radical, or removing or reducing the proportion of the positive radical of a compound.** Reduction is the converse.

Oxidation and Valence. — Combining a metal with oxygen or sulphur raises the *active valence* of the metal from zero to some finite value: $2Cu^0 + O_2{}^0 \rightarrow 2Cu^{II}O^{II}$. *Metallic* copper has *no valence in use.* In CuO or $CuCl_2$, it has become bivalent. The copper has been oxidized. Similarly, changing $FeCl_2$ into $FeCl_3$ increases the active valence of the iron from two to three (oxidation). Conversely, with non-metals, changing 2HCl to Cl_2 decreases the active valence of chlorine from one to zero (oxidation).

Again, in displacement, *e.g.*, $Zn + 2HCl \rightarrow ZnCl_2 + H_2$, the zinc is oxidized because the active valence goes from zero to two, and the hydrogen is reduced.

Hence, **oxidation** consists in **increasing the active valence of a positive element or decreasing that of a negative element (or radical).** Reduction is the converse.

Oxidation and Ionization. — If, in the last illustration, we write the equation ionically: $Zn + 2H^+ \rightarrow Zn^{++} + H_2$, we discover that, logically, we must consider the change from metallic zinc to zinc-ion to be in itself oxidation. Conversely, the discharge of the $2H^+$, giving H_2, is reduction. In the reaction: $2I^- + Cl_2 \rightarrow I_2 + 2Cl^-$, the iodide-ion is oxidized and the chlorine is reduced.

Thus, **ionization of an elementary substance to form a positive ion is oxidation,** and **ionization to form a negative ion is reduction,** and conversely.

Oxidation and Electrons. — Finally, since increasing the valence of a negative atom means adding one or more electrons to that atom, and increasing the positive valence of an atom means removing one or more electrons, we reach the *briefest* definition by saying: **Oxidation is removing electrons and reduction is adding electrons.**

Making Equations for Oxidations and Reductions. — The writing of equations for actions involving oxidation and reduction, *where there are more than two substances on one side of the equation,* is difficult (compare p. 239), and a system or plan is of great value. The plan of **positive and negative valences** is often applicable, but in most cases the equations may be much more neatly expressed in terms of **ions and electrons.**

Making Equations; Using Positive and Negative Valences. — Suppose we wish to balance the equation for the preparation of bromine by the action of manganese dioxide and concentrated sulphuric acid on sodium bromide (p. 345). We ascertain, in the laboratory, that the final products are free bromine, sodium-hydrogen sulphate, manganous sulphate and water:

Skeleton: $NaBr + MnO_2 + H_2SO_4 \rightarrow Br_2 + NaHSO_4 + MnSO_4 + H_2O.$

On examining the formulæ of the initial and resultant products in this equation, we find that *the valences of Br and Mn only have been affected.* On the left side, the valences of these elements are -1 and $+4$ respectively. On the right side, their valences have been changed to 0 and $+2$. Every bromine atom concerned in the reaction therefore loses in negative valence by 1, and every atom of manganese loses in positive valence by 2. In order to maintain equality of $+$ and $-$ valences, it is obvious that twice as many bromine atoms as manganese atoms must be involved. We may therefore start to complete our equation by writing 2NaBr in place of NaBr. This immediately requires the use of $2NaHSO_4$ on the right side of the equation, in order to balance up the sodium atoms. Our equation thus reads:

Incomplete: $2NaBr + MnO_2 + H_2SO_4 \rightarrow Br_2 + 2NaHSO_4 + MnSO_4 + H_2O.$

When we now count the number of sulphur atoms on the two sides, we see that we need to write $3H_2SO_4$ on the left to obtain equality. Having made this change, we have to write $2H_2O$ on the right, and then the quantities of all the elements present are correctly balanced. *Our equation is therefore complete.*

Balanced: $2NaBr + MnO_2 + 3H_2SO_4 \rightarrow Br_2 + 2NaHSO_4 + MnSO_4 + 2H_2O.$

Making Equations by Means of Ions and Electrons. — All oxidation reactions involving electrolytes can be written in terms of ions. Thus, the oxidation of hydrochloric acid by potassium per-

manganate can be so written. Potassium permanganate ionizes in solution to give the positive ion K^+ and the complex negative ion $(MnO_4)^-$. The potassium-ion clearly is not affected, and may be omitted. The substances actually concerned (see p. 239) are:

$$MnO_4^- + H^+ + Cl^- \rightarrow H_2O + Mn^{++} + Cl_2^0.$$

Cl_2^0 with no charge stands for free chlorine. Now we can divide the action into (1) the fate of the oxidizing agent, and (2) the fate of the substance being oxidized.

The fate of the oxidizing agent, since all the Mn in the MnO_4^- goes to Mn^{++} and all the O_4 goes to H_2O, in the formation of which $8H^+$ will evidently be required, is expressed by the equation:

Skeleton: $$MnO_4^- + 8H^+ \rightarrow Mn^{++} + 4H_2O.$$

This equation is already balanced, so far as the atoms of the various elements present are concerned, but when we examine the electrical charges on either side, we find that there is a deficiency of 7 equivalents of negative electricity on the left hand, and a deficiency of only 2 equivalents of negative electricity on the right. In the course of the reaction, therefore, each equivalent of the oxidizing agent has gained $7 - 2 = 5$ equivalents of negative electricity. In other words, *each unit of MnO_4^- has gained five electrons* (p. 313). The true balanced equation is, consequently:

Balanced: $$MnO_4^- + 8H^+ + 5\ominus \rightarrow Mn^{++} + 4H_2O. \quad (1)$$

We understand where these electrons came from when we consider the fate of the chlorine. The change from Cl^- to Cl_2 may be expressed:

$$2Cl^- \rightarrow Cl_2^0 + 2\ominus. \quad (2)$$

In order to balance out the electrons in equations (1) and (2), we evidently require to multiply equation (1) by 2 and equation (2) by 5 throughout. When we do this, and add the two equations together in order to represent both the reduction of the manganese and the oxidation of the chlorine in a single equation, we obtain the final answer to our problem in the statement:

$$2MnO_4^- + 16H^+ + 10Cl^- \rightarrow 2Mn^{++} + 8H_2O + 5Cl_2^0.$$

The student should compare this with the equation previously deduced on p. 239, and convince himself of their essential identity.

The chief advantages of the above method are as follows: (*a*) the final equation contains only substances which have *actually undergone a change* in the reaction; (*b*) equations (1) and (2) represent *the oxidation and reduction reactions which actually occur at the electrodes* when the experiment is conducted in a battery-cell as a source of electrical energy (see p. 839); and (*c*) the method does not lead to incorrect results in the case of "trick" compounds such as H_2O_2. The representation is, therefore, more accurate from a practical viewpoint, and at the same time it furnishes us with a much clearer idea of the mechanism of electrochemical reactions. Additional examples of the application of this method to complex oxidation-reduction reactions will be presented for the student to solve in subsequent chapters.

The valence method is to be preferred, in general, only when the reaction under consideration is not practicable from the electrochemical side. An example is the reaction (p. 386):

$$4KClO_3 \rightarrow 3KClO_4 + KCl.$$

The student is apt to underestimate the importance of the above sections, because he thinks that he can memorize the reactions discussed, or balance them by repeated trials, with less difficulty than is involved in the mastery of the recommended methods. He should recognize, however, that these methods are going to be of continuous service to him throughout the rest of his chemical career. It took longer to build a railroad from New York to San Francisco than it would have taken to walk the same distance, but that is no valid argument against the use of railroads.

Exercises. — 1. What volume of ozone will be taken up by 100 c.c. of water at 12° from a stream of oxygen containing 7.5 per cent of ozone (pp. 220, 363)?

2. At what temperature (approximately) will an aqueous solution of hydrogen peroxide, containing 10 g. of the substance to 1000 g. of water, freeze (pp. 217, 368)?

3. Write the thermochemical equation for the (theoretical) oxidation of indigo by hydrogen peroxide (pp. 366, 369).

4. What volume (at 0° and 760 mm.) of oxygen would be obtained by the decomposition of the hydrogen peroxide in 1 kilogram of the 3 per cent solution?

5. Why does a given weight of chlorine in the form of hypochlorous acid have twice as great a bleaching (or oxidizing) capacity as has the same weight of chlorine in chlorine water?

6. How should you make pure potassium hypochlorite from chlorine-water?

7. Classify the following changes as oxidations or reductions: (*a*) $H_2Cr_2O_7 \rightarrow H_2CrO_4 + CrO_3$; (*b*) $HMnO_4 \rightarrow MnO_2$; (*c*) $I_2 \rightarrow 2I^-$; (*d*) $2H_2O_2 \rightarrow 2H_2O + O_2$; (*e*) $Zn \rightarrow Zn^{++}$.

8. Apply the positive and negative valence method of writing equations to the action of HCl on $KMnO_4$.

9. Apply the ion and electron method of writing equations to: (*a*) the action of manganese dioxide and concentrated sulphuric acid on sodium bromide; (*b*) the action of HCl on $K_2Cr_2O_7$.

10. Sodium peroxide cannot be vaporized without decomposition. What reasons have we for writing its formula as Na_2O_2 rather than NaO?

11. What substances act as "negative catalysts" in the decomposition of hydrogen peroxide? Can you think of other cases of negative catalysis in chemistry?

12. From the following thermochemical data, calculate the heat of formation of liquid H_2O_2 (*i.e.*, the heat effect of the imaginary reaction: $H_2 + O_2 \rightarrow H_2O_2$):

$$2H_2 + O_2 \rightarrow 2H_2O \text{ (gas)} + 116{,}200 \text{ cals.}$$
$$H_2O \text{ (gas)} \rightarrow H_2O \text{ (liquid)} + 9{,}800 \text{ cals.}$$
$$2H_2O_2 \rightarrow 2H_2O \text{ (liquid)} + O_2 + 46{,}200 \text{ cals.}$$

13. Devise a method of demonstrating that hydrogen peroxide is much more unstable in alkaline than in acid solution.

14. Three samples of water, colored faintly blue with indigo, are taken in separate test glasses. Through the first ozonized air is bubbled. To the second hydrogen peroxide is added. Through the third chlorine gas is passed. What do you observe in each case? How do you account for any differences?

15. Tabulate *all* of the substances that may be present in a solution of chlorine in water under various conditions of temperature and pressure (pp. 245, 371). Write equations to show the mode of formation of each. [*Note:* You ought to be able to list at least a dozen substances. Do not forget ionization.]

16. Why does absolutely dry chlorine bleach a carnation? Why does a solution of chlorine in water, after exposure to sunlight for some time, exhibit no bleaching power?

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CHAPTER XXII

OXIDES AND OXYGEN ACIDS OF THE HALOGENS

The chief subjects of practical importance touched upon in this chapter are connected with potassium chlorate $KClO_3$ and perchlorate $KClO_4$. Hence our attention will be largely directed to the modes of making these substances and to their relations to one another. Incidentally, we shall encounter several actions of a complex and, to us, more or less novel kind.

Compounds of Chlorine Containing Oxygen. — The following are the names and formulæ of the main parent substances:

$HOCl$ Hypochlorous acid,	Cl_2O Hypochlorous anhydride,
$[HClO_2]$ Chlorous acid,	. . . .
. . . .	ClO_2 Chlorine dioxide,
$HClO_3$ Chloric acid,	. . . .
$HClO_4$ Perchloric acid,	Cl_2O_7 Perchloric anhydride.

There are also salts of these acids, like the two substances mentioned in the first paragraph. Chlorous acid is itself unknown, but potassium chlorite $KClO_2$ and some other derivatives have been made.

The two anhydrides (p. 174), when brought into contact with water, combine with it to form the acids opposite which they stand in the table. Chlorine dioxide, however, is not related to any one acid in this way. Two less important oxides, Cl_2O_6 and Cl_2O_8, are similar to chlorine dioxide in this respect.

All these compounds differ from most that we have hitherto discussed, inasmuch as not one of them can be made by direct union of the simple substances.

Relation of Anhydride and Acid or Salt. — The derivation of the formula of the anhydride from that of the acid or salt should receive special attention. In the mind of the chemist, the one always instantly suggests the other, so often does he think of them as potentially the same substance. The beginner, however, finds this habit hard to acquire, and indeed is more likely to blunder,

in trying to divide the formula of an acid into the formulæ of water and the anhydride, than in any other calculation he makes.

The rule is: If the formula of the acid shows an *even* number of hydrogen atoms (H_2SO_4 or H_4SiO_4), subtract all the elements of water (H_2O or $2H_2O$), and the balance is the anhydride (SO_3 or SiO_2). The divided formulæ are H_2O,SO_3 or $2H_2O,SiO_2$. If there is an odd number of hydrogen atoms ($HClO_4$ or H_3PO_4) *double* the formula ($H_2Cl_2O_8$ or $H_6P_2O_8$), and subtract all the elements of water as before (Cl_2O_7 or P_2O_5). Then check the result, by adding the water again, and dividing by two, correcting the blunder if one has been made.

If the substance is a salt ($CuSO_4$ or $KClO_4$), subtract the oxide of the metal (CuO or K_2O), taking care to assign to the metal the same valence in the oxide as it shows in the salt.

There are several uses for this art of ascertaining the anhydride corresponding to a given salt or acid. One is in the making of equations involving the anhydride. Another is in finding the valence of the non-metal. Thus, in $KClO_4$ the anhydride is Cl_2O_7, and the valence of the chlorine is seven. In H_3PO_4 the anhydride is P_2O_5 and the phosphorus quinquivalent. In HPO_3 (metaphosphoric acid), the anhydride is again P_2O_5, and the phosphorus is therefore in the same state of oxidation — both are phosphor*ic* acids.

Nomenclature. — The acids and salts *within one group* are distinguished by the terminations of, and prefixes to, their names. Thus we have:

*Hydro*chlor*ic* acid	HCl	Sodium chlor*ide*	$NaCl$
*Hypo*chlor*ous* acid	$HOCl$	Sodium *hypo*chlor*ite*	$NaOCl$
Chlor*ous* acid	$HClO_2$	Sodium chlor*ite*	$NaClO_2$
Chlor*ic* acid	$HClO_3$	Sodium chlor*ate*	$NaClO_3$
*Per*chlor*ic* acid	$HClO_4$	Sodium *per*chlor*ate*	$NaClO_4$

The proportion of oxygen to the other elements is at the basis of the system. The terminations *ous* and *ite* indicate less oxygen than *ic* and *ate*. The prefix *hypo* (Greek, *below*) implies still less oxygen, the prefix *hydro* implies none at all. The *per*-acid contains the most oxygen.

It should be noted, however, that the use of *ic* and *ous* for more and less oxygen, respectively, and of *hypo* for still less and of *per* for still more oxygen are simply relative terms *within a single group*. Thus, sulphur*ic* acid H_2SO_4 has a structure entirely different from chlor*ic* acid, and both of these differ in construction from phosphor*ic* acid H_3PO_4. The names and formulæ of each group must be learned, separately.

The properties of hypochlorous acid and of hypochlorites have already been considered in detail in the preceding chapter.

Chlorates. — Like hypochlorous acid itself (p. 371), the hypochlorites are readily converted, in part, into chlorates. Thus, when chlorine is passed into a *warm*, concentrated solution of potassium hydroxide, and particularly when an excess of chlorine is used, the potassium hypochlorite changes into **potassium chlorate** $KClO_3$ as fast as it is formed. Since this action (equation 2) requires 3KOCl, the equation formerly given (p. 374) must be tripled:

$$3Cl_2 + 6KOH \rightarrow 3KCl + 3KOCl + 3H_2O \qquad (1)$$

$$3KOCl \rightarrow 2KCl + KClO_3 \qquad (2)$$

Adding: $$3Cl_2 + 6KOH \rightarrow 5KCl + KClO_3 + 3H_2O$$

When the solution is cooled, the less soluble chlorate crystallizes out.

This action involves converting five-sixths of the valuable potassium hydroxide into the relatively less valuable potassium chloride. Hence, in practice, the makers carry out the corresponding action with calcium hydroxide. They then add potassium chloride to the resulting solution, containing calcium chloride (very soluble) and **calcium chlorate** $Ca(ClO_3)_2$. The potassium chlorate, formed by double decomposition, crystallizes out when the solution is cooled.

Large quantities of chlorates are also manufactured now by electrolytic methods. The procedure is as in the preparation of hypochlorites (p. 374), but instead of keeping the chloride solution neutral and at a low temperature, either hydrochloric acid or alkali is added and the temperature raised. Under such conditions, almost perfect yields of chlorate can ultimately be obtained.

All chlorates are at least moderately soluble in water (see table inside of front cover). Potassium chlorate is **used** in making fireworks, explosives, and matches. An intimate mixture with sugar $C_{12}H_{22}O_{11}$ burns with semi-explosive violence, the oxygen of the salt combining with the carbon and hydrogen of the sugar to form carbon dioxide and water.

The Separation of Substances by Their Solubility. — When neither of the products of an action approaches absolute insolubility, a separation may nevertheless be effected more or less perfectly by taking advantage of differences in solubility. Thus, in the practical method of making potassium chlorate, the calcium chloride is exceedingly soluble, while the potassium chlorate is only moderately so. Then, too, the solubility of the latter decreases rapidly as the temperature is lowered (Fig. 87, p. 206). Hence, it is found that when the mixture is cooled to − 18° only about 13.5 g. of potas-

sium chlorate remain dissolved in each liter, and are lost. At 0° the loss would be greater, for at this temperature a liter of pure water would retain 33.3 g.

It will be seen that we reason as if the solubility of each substance was independent of the presence of the other dissolved product. This is not always justified in actual practice (see p. 757), but serves as a first approximation.

By the use of this principle, and the data in regard to solubility in Fig. 87 (p. 206), a rough idea may be obtained of what may be expected in any given case. From the diagram the solubilities at any given temperature may be read. Suppose, for example, the question is in regard to the quantity of potassium chlorate we may expect to obtain from 3 g. of potassium hydroxide dissolved in 7 g. of water (a 30 per cent solution). From the equation:

$$\underset{6 \times 56}{3Cl_2 + 6KOH} \rightarrow \underset{122.5}{KClO_3} + \underset{5 \times 74.5}{5KCl} + \underset{3 \times 18}{3H_2O}$$

we find that 336 g. of potassium hydroxide give 122.5 g. of chlorate, 372.5 g. of chloride and 54 g. of water. Hence, by proportion, 3 g. will give 1.1 g., 3.3 g. and 0.5 g. respectively. The solubility, read from the diagram, is the amount of the salt dissolved by 100 g. of water, for example, 56.5 g. of potassium chloride at 100°. In the system here under consideration, the total amount of water present at the end of the reaction is 7.5 g., and some of the solubility results at different temperatures are given in the form of a table:

		Potassium Chloride	Potassium Chlorate
Amount formed from 3 g. KOH		3.3	1.1
Solubility at 100° in	100 g. Water	56.5	56.5
	7.5 g. Water	4.2	4.2
Solubility at 20° in	100 g. Water	34.7	7.5
	7.5 g. Water	2.6	0.6
Solubility at 0° in	100 g. Water	28.0	3.3
	7.5 g. Water	2.1	0.25

Thus, at 20°, about 2.6 g. of the 3.3 g. of potassium chloride will remain dissolved, while nearly half of the potassium chlorate will crystallize out. By a second crystallization, a small amount of pure potassium chlorate will be obtained. If the solubilities are examined, however, it will be seen that the potassium chlorate is much more easily obtainable in pure condition when calcium chloride takes the place of potassium chloride.

Chloric Acid $HClO_3$. — This acid may be obtained, in solution in water, by adding the calculated amount of diluted sulphuric acid to a solution of barium chlorate:

$$Ba(ClO_3)_2 + H_2SO_4 \leftrightarrows BaSO_4 \downarrow + 2HClO_3.$$

The barium sulphate, being insoluble, is removed by filtration. It will be noted that **double decomposition, involving precipitation, may thus be used for obtaining a soluble product,** as well as an insoluble one (compare hydrogen peroxide, p. 367).

The solution may be concentrated (to about 40 per cent) by evaporation, but must not be heated above 40°, as the acid decomposes near this temperature. The resulting thick, colorless liquid has powerful oxidizing qualities, even setting fire to paper (p. 600) which has been dipped into it. It converts iodine into iodic acid, $2HClO_3 + I_2 \rightarrow 2HIO_3 + Cl_2$. When warmed beyond 40° the acid decomposes, giving **chlorine dioxide** and **perchloric acid:**

$$3HClO_3 \rightarrow H_2O + 2ClO_2 + HClO_4.$$

The anhydride corresponding to chloric acid, Cl_2O_5, is not known.

Chlorine Dioxide. — **Chlorine dioxide** ClO_2 is a yellow gas which may readily be liquefied (b.-p., + 10°). The gas and liquid are violently explosive, the substance being resolved into its elements with liberation of much heat. It is formed whenever chloric acid is set free, and hence it is seen when a little powdered potassium chlorate is touched with a drop of concentrated sulphuric acid on a glass rod.* Concentrated hydrochloric acid turns yellow from the same cause when any chlorate is added to it. These actions are used as **tests** for chlorates, and distinguish them from perchlorates. With water, chlorine dioxide gives a yellow solution which is without acid reaction but gives with bases a mixture of the **chlorite** and chlorate. The chlorites of the alkali metals act as bleaching agents, but have no industrial importance.

Perchlorates. — When heated, chlorates give **perchlorates.** Chlorates also give oxygen at the same time (p. 91):

$$\begin{cases} 2KClO_3 \rightarrow 2KCl + 3O_2, \\ 4KClO_3 \rightarrow 3KClO_4 + KCl. \end{cases}$$

These actions, like the three decompositions of hypochlorous acid (p. 371), are independent, and proceed simultaneously. They are **concurrent** reactions (see p. 388). Their relative speed, however, varies with the temperature, and the decomposition into chloride and oxygen may completely outrun the other when a catalytic agent like manganese dioxide is added (p. 103). When pure potassium chlorate is heated cautiously, about one-fifth of it has lost

* The mixture of sugar and potassium chlorate (p. 384) can be set on fire by a drop of sulphuric acid. The latter liberates chloric acid, which in turn gives ClO_2, and this, being a violent oxidizing agent, starts the combustion of the sugar.

all its oxygen by the time the rest has turned into perchlorate. The mixture may be separated by grinding with the minimum quantity of water which will dissolve the chloride it contains. The perchlorate, having at 15° less than one-twentieth of the solubility of the chloride, will remain, for the most part, undissolved. The perchlorates are much more stable (p. 392) than the chlorates or hypochlorites, they are all soluble in water, and they are used in making matches and fireworks. When heated strongly, they decompose and leave the chlorides.

Perchlorates are mainly manufactured now by the high current-density electrolysis of chlorate solutions. Since sodium chlorate is highly soluble, sodium perchlorate is generally prepared first. This salt, however, being deliquescent, is unsuitable for use in fireworks or explosives, and the potassium or ammonium salt is obtained therefrom by double decomposition (compare p. 384).

Perchloric Acid $HClO_4$ and Perchloric Anhydride Cl_2O_7. – Pure **perchloric acid** is a liquid which explodes when heated abo 92°. But, like other liquids, its boiling-point is lower when its va *is under reduced pressure* (compare p. 367). At 56 mm. pressure it boils at 39°, a temperature at which hardly any decomposition is noticeable. Hence the acid may be made by passing HCl gas through a saturated solution of sodium perchlorate, decanting off the clear liquid from the precipitate of less soluble sodium chloride that is formed (compare p. 385), and distilling cautiously under a low pressure:

$$NaClO_4 + HCl \rightleftarrows NaCl\downarrow + HClO_4.$$

The pure acid decomposes, and often explodes spontaneously, when kept. A 70 per cent solution in water is perfectly stable, however. Although it is an active oxidizing agent, it is not so active as chloric acid, and does not oxidize hydrogen chloride in cold aqueous solution. Hence a drop of hydrochloric acid placed on a crystal of a perchlorate gives no yellow color. When the acid is liberated by concentrated sulphuric acid, it does not at once give the yellow chlorine dioxide (p. 386).

Perchloric anhydride Cl_2O_7 may be prepared by adding phosphoric anhydride to perchloric acid in a vessel immersed in a freezing mixture, $P_2O_5 + 2HClO_4 \rightarrow 2HPO_3 + Cl_2O_7$. Phosphoric anhydride is often used in this way for removing the elements of water from compounds. It combines with the water to form metaphos-

phoric acid HPO_3. By gently warming the mixture, the perchloric anhydride can be distilled off. It is a colorless liquid boiling at 82° (760 mm.) and exploding when struck or too strongly heated.

Concurrent and Consecutive Reactions. — When two or more reactions go on simultaneously in the same materials, the actions may be parallel or they may be consecutive. In the former case they are called **concurrent reactions.** Thus, hypochlorous acid undergoes three different changes:

$$2HOCl \rightarrow H_2O + Cl_2O.$$
$$3HOCl \rightarrow HClO_3 + 2HCl.$$
$$2HOCl \rightarrow 2HCl + O_2.$$

Some molecules decompose into water and chlorine monoxide (p. 371), while others give chloric acid and hydrogen chloride, and still others hydrogen chloride and oxygen. Since the *same molecule* cannot undergo more than one of these different changes, it follows that the actions are independent of one another. This is shown by the fact that in sunlight the third predominates, while in the dark it falls far behind the second. Since the *relative* quantities of the products vary, the **several simultaneous actions cannot be put in the same equation.** The fundamental property of an equation is to show the *constant* proportions by weight between every pair of substances in it. Hence separate equations for each reaction are required in this case, and in all similar cases where all the proportions are not constant. Thus, again, in the decomposition of potassium chlorate by heating (p. 386), it would be misleading and wrong to add the two equations together and write, for the whole action:

$$2KClO_3 \rightarrow KCl + KClO_4 + O_2.$$

This equation would mean that the proportions amongst the products were always $KCl : KClO_4 : O_2$ or 74.56 : 138.56 : 32, whereas, in fact, the proportions vary with the conditions — the temperature used or the presence of a catalyst which hastens one action but not the other.

Consecutive reactions, however, like (1) followed by (2) on p. 384, may properly be combined in one equation, since in them all the proportions must necessarily be constant. These equations are interlocked, for (2) consumes the intermediate products that (1) produces. It may be noted that if the second action is as speedy

as the first, or speedier, then no intermediate products will be detectable (see p. 423).

A very striking lecture illustration of this last point may be arranged as follows: 1 c.c. of 0.5 *N* iodic acid solution * is added to 100 c.c. of filtered starch emulsion (p. 602) in one flask. 1 c.c. of 0.5 *N* sulphurous acid solution † is added to 100 c.c. of water in a second flask. The contents of the two flasks are mixed as rapidly and as thoroughly as possible, and the time noted on a stop-watch. Nothing visible occurs for more than a minute. Then, in a flash, the whole solution suddenly turns a deep blue.

This mysterious behavior is readily explained on the basis **of consecutive reactions.** There are *three* such reactions taking place in the solution:

$$HIO_3 + 3H_2SO_3 \rightarrow HI + 3H_2SO_4 \quad (1)$$
$$HIO_3 + 5HI \rightarrow 3H_2O + 3I_2 \quad (2)$$
$$I_2 + H_2SO_3 + H_2O \rightarrow H_2SO_4 + 2HI. \quad (3)$$

Now the quantities of the original substances taken were intentionally fixed so as to have HIO_3 in excess. Reaction (1), producing HI, is fairly slow. Reaction (2), producing I_2, is rather more rapid. Reaction (3), using up the I_2 produced in (2), is very much faster. Consequently, so long as any appreciable amount of H_2SO_3 is left in the solution, no iodine can be detected, since it is consumed as quickly as it is formed. But as soon as all H_2SO_3 is exhausted, reaction (3) can no longer continue, and the iodine liberated in reaction (2) immediately makes itself evident by giving its distinctive coloration with starch (p. 350).

Chain Reactions. — A particularly interesting type of consecutive reactions is afforded by what are known as *chain reactions.* A good example is the combination of hydrogen and chlorine, which occurs at low temperatures only in the presence of light (p. 243). The function of the light is to furnish energy for the dissociation of molecular chlorine into activated chlorine atoms. A chain of reactions is thus initiated:

$$Cl + H_2 \rightarrow HCl + H,$$
$$H + Cl_2 \rightarrow HCl + Cl,$$

which can obviously continue indefinitely so long
not broken.

In practice, it has been found that the activa

* This may most conveniently be prepared by dissolving potassium iodate KIO_3 in water, adding an equivalent quan
a standard solution, and diluting with water until the solu
respect to each.

† This may most readily be made by dissolving a known
bisulphite in freshly-boiled water, and diluting to the requ

chlorine atom may suffice for the production of 10^4 molecules of HCl. The chain may be broken in several ways — chlorine or hydrogen atoms may become immobilized on the wall of the reaction vessel, they may meet each other and end two chains by the reaction $H + Cl \rightarrow HCl$, or they may interact with impurities present in the mixture. In this last connection it may be noted that the introduction of a trace of oxygen into the system slows the reaction down tremendously. The mechanism of this and of many other instances of *negative catalysis* is clearly the breaking of a chain.

Oxides and Oxygen Acids of Bromine. — The only known oxides of bromine are Br_2O, identified in the reaction between bromine and specially-prepared mercuric oxide, and Br_3O_8, recently obtained in the form of white crystals by the action of pure (100 per cent) ozone on pure bromine vapor at a low temperature and pressure. The acids HOBr (hypobromous acid) and $HBrO_3$ (bromic acid) and their salts, however, are more familiar.

By the action of bromine on dilute, cold potassium hydroxide solution, **potassium bromide** and **hypobromite** are formed:

$$Br_2 + 2KOH \rightarrow KBr + KOBr + H_2O.$$

When the solution is heated, the hypobromite turns into **potassium bromate** and bromide. The actions are exact parallels of the corresponding ones for the hypochlorite (pp. 374, 384).

Aqueous **bromic acid** $HBrO_3$ may be made in the same way as chloric acid (p. 385). The solution is colorless and has powerful oxidizing properties. Thus, like chloric acid, it converts iodine into iodic acid: $2HBrO_3 + I_2 \rightarrow 2HIO_3 + Br_2$.

Oxi **Oxygen Acids of Iodine.** — There are four oxides,
, and IO_4. The only one of importance is I_2O_5,
l in water, gives iodic acid, HIO_3. **Sodium iodate**
n Chile saltpeter. Hypo-iodites and per-iodates are

IO_3, the most important oxygen acid of iodine, is
rmed by passing chlorine through iodine suspended

$$HOCl + H_2O + I_2 \rightarrow 2HIO_3 + 5HCl.$$

ay is to boil iodine with aqueous nitric acid HNO_3

(see p. 533). The latter gives up oxygen readily, and is here reduced to nitric oxide NO:

$$3I_2 + 10HNO_3 \rightarrow 6HIO_3 + 10NO + 2H_2O.$$

(The student should try himself out upon both of the above equations by the methods indicated on pp. 378–9, starting with the skeletons as in Exercise 9, p. 395. In both these actions the initial substances (including the excess of nitric acid) and the products, with the exception of the iodic acid itself, are all volatile. When the solution is concentrated by evaporation, therefore, only the iodic acid crystallizes. It is a white solid, perfectly stable at ordinary temperatures, and can be kept indefinitely. At 170° it begins to give off water vapor ($2HIO_3 \rightleftarrows H_2O + I_2O_5$), leaving **iodic anhydride.** The latter is a white crystalline powder which may be raised to 300° before it, in turn, breaks up, giving iodine and oxygen.

Various Acids from One Anhydride; Periodic Acid. — Some acids are related to their anhydrides as are hypochlorous acid (p. 371) and sulphurous acid (p. 415). One molecule of the anhydride combines with one molecule of water. In other cases, however, the proportion of water may be less or greater than this. Now if **periodic acid** were of the former type ($H_2O,I_2O_7 = 2HIO_4$), its formula would be HIO_4. It does form *salts* of this type, such as $NaIO_4$ and $AgIO_4$. But the free acid is a deliquescent solid of the formula H_5IO_6 ($= 5H_2O,I_2O_7$), and the most easily prepared salt $Na_2H_3IO_6$ (see below) belongs to this type. *All types are called periodates, however, because their compositions are all founded upon the same anhydride.* The latter has not itself been made. We usually speak of various acids and salts as being **derived from** the same anhydride, the word "derived" being used in a figurative and not a literal sense.

The difference between the two acids HIO_4 and H_5IO_6 is not at all the same as between HIO_3 and HIO_4. The latter would represent different stages of oxidation, being derived from I_2O_5 and I_2O_7, respectively, and accordingly would be named iodic acid and periodic acid. The former differ only by $2H_2O$, and an addition or subtraction of the elements of water *in equivalent quantities* is neither oxidation nor reduction. Hence they are both periodic acids (compare Phosphoric acid, pp. 383, 550).

Sodium periodate $NaIO_4$ is found in Chile saltpeter (p. 504).

When sodium iodate $NaIO_3$ is dissolved along with sodium hydroxide in water, and chlorine is passed into the mixture as an oxidizing agent, the somewhat insoluble salt which crystallizes out is $Na_2H_3IO_6$. Other salts may be made from this one.

An aqueous solution of **periodic acid** is obtained by the action of sulphuric acid on barium periodate, followed by filtration. A white, very soluble solid H_5IO_6 remains when the liquid is evaporated. When this is heated, water and oxygen are both given off, and iodine pentoxide I_2O_5 alone remains.

Oxides and Oxygen Acids of Fluorine. — The compound F_2O has already been noted (p. 356). A gaseous oxide FO and a yellow solid F_2O_2 have also been claimed to exist.

No oxygen acids of fluorine have been isolated, but some evidence exists for the presence of hypofluorites and fluorates in aqueous solution.

Chemical Relations. — The compounds of the halogens with metals and with hydrogen diminish in stability, with ascending atomic weight of the halogen. Each halogen will displace those following it from *this kind* of combination. In the case of the oxygen compounds, however, the order of stability is just the reverse, those of iodine, for example, being the only ones which are reasonably stable.

Amongst the oxygen acids of any one halogen, those containing most oxygen are most stable. The salts are in all cases more stable by far than the corresponding acids. The oxygen acids and salts of fluorine are all too unstable for isolation.

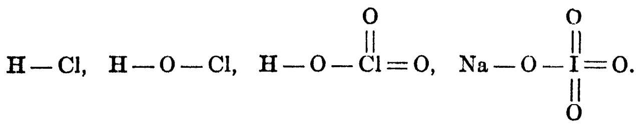
The halogens when combined with metals and hydrogen are univalent (HI, KCl, etc.). It is clear, however, that, when united with oxygen, their valence is usually higher. The maximum is shown in perchloric anhydride (Cl_2O_7), where chlorine appears to be septivalent.

The formulæ of the acids *might* all be written so as to retain univalence:

$$H—Cl,\ H—O—Cl,\ H—O—O—Cl,\ H—O—O—O—Cl,$$
$$H—O—O—O—O—Cl.$$

But compounds in which we are *compelled* to believe that two oxygen units are united are usually unstable (*e.g.*, hydrogen peroxide, H — O — O — H), and we should expect the instability would be greater with three and with four units of oxygen in combination. Here, however, the reverse state of affairs must be taken account of in our formulæ, for $HClO_4$ is the most stable of the chlorine set. This reasoning, together with the septivalence suggested in Cl_2O_7, leads us to assume the valence seven in perchloric acid (see Periodic

System). The graphic formulæ (see p. 146) of some of these substances are therefore written as follows:



The Specification of Chemical Properties. — The chemical properties of a substance are frequently specified so loosely that the student has no definite guide before him. The following illustrates the scheme that should be kept in mind.

1. **Stability** (p. 173), particularly if a compound, but applicable also to elements like iodine (p. 351). Mention products of decomposition.
2. **Molecular weight,** if known.
3. **Class to which the substance belongs,** and indication of degree of activity where possible, such as simple substance, weak acid, strong base, salt, carbohydrate, etc. Terms like acid, base, and salt imply certain properties, which need not be given in detail.
4. **Substances with which combination occurs,** such as the metals (exceptions named), the non-metals (exceptions named), water, ammonia, etc. The class to which the resulting compounds belong should be named.
5. **Oxidizing or reducing agent,** if such, with illustrations and indication of limitations.
6. **Other specific chemical reactions,** such as hydrolysis, if a salt; action of chlorine, if a hydrocarbon; etc.

Each chemical property should specify directly (or by implication, *e.g.,* by using the word *acid,* see p. 131) **some definite variety of chemical change, or kind of chemical behavior,** and should name the materials or classes of materials involved.

The **chemical relations** are **not** properties of a *substance,* but qualities of an element in combination, such as atomic weight, valence, non-metallic or metallic element (oxide acidic or basic, halides hydrolyzed or not). They have been discussed elsewhere (pp. 247, 445).

It may be well to illustrate inept ways of giving chemical properties. "Oxygen supports combustion of a candle." The beginner does not know that a candle is composed of a cotton wick surrounded by a mixture of hydrocarbons and fatty acids, so no chemical reaction can be extracted by him from this statement. The chemical property is the tendency of compounds of carbon and hydrogen to interact vigorously with oxygen, giving water and carbon dioxide. The burning of a candle for light is an *application* of this property, *but is not the property itself.* Applications should be given, of course, but they should follow the property, not displace it. Similarly, "bleaching ability" is often given as a chemical property. But sodium hyposulphide and other substances bleach indigo by reducing it to indigo white, and hypochlorous acid and ozone bleach indigo by oxidizing it to isatin, sodium hydroxide bleaches blue prints because it is an active base and interacts with the ferrous ferricyanide, and water and other solvents sometimes bleach by dissolving the dye. Bleaching may, therefore, be due to entirely different chemical or physical properties in different cases. It is an *application* of some specific chemical property, and should be given as an illustration of the use of the property.

Similarly, "disinfecting power" in the case of hypochlorous acid or hydrogen peroxide is due to oxidation of the unstable substances in the pathogenic organisms, but sulphurous acid adds itself to the aldehydes which their protoplasm contains, alcohol (used, *e.g.*, to sterilize the skin before vaccination) takes the place of the moisture in the organisms, killing them by physical means, and formaldehyde is a reducing agent, and is also able to add itself to, or to give condensations with, many organic compounds. Disinfecting power is thus *an application* of one of the foregoing, or of some other property, which should first be specified. When a substance is poisonous, this should be emphasized, but not given as a chemical property. Even when the chemical changes, which the poisons bring about in the body, are known, they can seldom be explained in inorganic or elementary general chemistry.

Again the phrase "supports combustion" is of uncertain meaning. In ordinary language it refers to fuels like wood and coal. To say that "chlorine supports combustion," is, therefore, not specific enough. Coal and wood will not burn in it. Iron, copper, and antimony will, but if these substances are not named, the statement leaves the reader to supply the very information which he lacks, and which the book should have furnished. Still again, the statement that chlorine combines with copper and sodium omits to make it clear that chlorine combines easily with all the familiar metals, excepting platinum and gold. If each individual element with which chlorine combines is to constitute a separate chemical property, then, with only two elements named, the list of this class of properties is very incomplete, since it includes only two out of about seventy. Naming the *class* of elements, with illustrations and exceptions, covers the point, and puts less strain upon the memory.

Negative statements convey little information. "Nitrogen will not support combustion." This means, either that coal and tapers will not burn in it, in which case it should be explained that carbon and hydrogen do not readily unite with nitrogen, or else that nitrogen is not oxygen! Chemical properties should be stated positively, not reached indirectly, by excluding one by one all the things the substance cannot do. Nitrogen does not bleach, does not burn, and can neither climb a tree nor eat grass — but a hundred negative items will still leave us ignorant of what it *can* do. When two elements are very similar, yet one has a property which the other lacks, it is instructive, and therefore desirable, to mention the absence of the property, but such cases are rare. To parade as a property of phosphorus pentoxide that it is not combustible, is like saying that a bankrupt cannot pay his debts — it is redundant. Even more absurd is the statement, when given as a property, that chlorine is formed by oxidation of hydrochloric acid. This is a property of the acid and oxidizing agent. Chlorine has no properties as a substance until after it has been formed.

Exercises. — 1. Assign to its proper class (p. 232) each of the actions mentioned in this chapter.

2. Knowing that potassium fluosilicate K_2SiF_6 is insoluble, how should you make chloric acid (p. 385)?

3. Make the equation for the interaction of chlorine with calcium hydroxide in hot water (p. 384). How should you make zinc chlorate from zinc hydroxide $Zn(OH)_2$?

4. On what circumstances would the possibility of making barium chlorate by the action of chlorine on barium hydroxide depend (pp. 384–5)? Could

pure barium chlorate be obtained easily by this means (see Table of Solubilities)?

5. Make the equations for: (*a*) the preparation of potassium bromate; (*b*) pure aqueous bromic acid; (*c*) the interaction of iodine with aqueous potassium hydroxide in the cold, and (*d*) when heated.

6. Make the equations for the interactions of chlorine dioxide with water and with aqueous potassium hydroxide.

7. Find the formulæ of the anhydrides of the following acids: HPO_3, H_2SeO_4, H_3AsO_3, H_3AsO_4, H_6SO_6.

8. Find the formulæ of the anhydrides of the acids from the following formulæ of salts: Na_2SiO_3, Na_2HPO_4, NaH_2PO_3, $Na_2H_3IO_6$.

9. Apply each of the two methods (pp. 378–9) of writing complex equations to balance the following skeleton reactions:

(*a*) $HClO_3 \rightarrow H_2O + ClO_2 + HClO_4$.
(*b*) $KClO_3 \rightarrow KClO_4 + KCl$.
(*c*) $HOCl + H_2O + Br_2 \rightarrow HBrO_3 + HCl$.
(*d*) $HBrO_3 + I_2 \rightarrow HIO_3 + Br_2$.
(*e*) $I_2 + HNO_3 \rightarrow HIO_3 + NO + H_2O$.

10. What weight of potassium chlorate will be obtained by the action of excess chlorine on 500 c.c. of 6 *N* potassium hydroxide (warm), assuming that only a 80 per cent recovery of the pure salt is possible?

11. What weight of potassium chlorate would we require to take to obtain 20 g. of pure potassium perchlorate, assuming that one-fifth of our original material goes through the useless reaction $2KClO_3 \rightarrow 2KCl + 3O_2$, and that one-quarter of our $KClO_4$ formed is lost in the course of its purification?

12. Write the structural formulæ for potassium hypobromite, potassium chlorite, calcium bromate, calcium per-iodate, iodic anhydride, perchloric anhydride.

13. Why do hydrogen and chlorine molecules not interact directly, but only when activated by light (see pp. 264, 351)?

READING REFERENCE

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CHAPTER XXIII

SULPHUR AND HYDROGEN SULPHIDE

Sulphur, the compounds of which have been so often mentioned, provides us, in sulphuric acid, with a substance which has more extensive and more important applications in commerce than any other chemical. The element sulphur, itself, enters, with potassium nitrate and charcoal, into gunpowder. Vulcanite is a compound of caoutchouc (rubber) and sulphur. Sulphur is employed to destroy fungi on grape-plants, and furnishes sulphur dioxide for bleaching and disinfecting, as well as for use in paper manufacture (see Fig. 119).

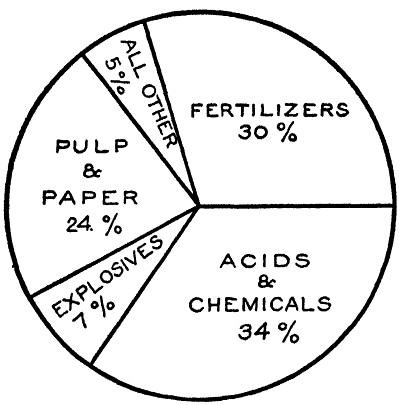


FIG. 119. Distribution of Sulphur in Industry.

Occurrence. — **Free sulphur** is found in volcanic regions in Sicily, where it is mixed with gypsum and other minerals and occupies the pores of pumice-stone. More extensive subterranean deposits exist in Texas and in Louisiana. There are many minerals, compounds containing sulphur, which are chiefly important on account of their other constituents. Sulphides of metals, such as **pyrite** FeS_2, **copper pyrites** $CuFeS_2$, **galena** PbS, **zinc-blende** ZnS, and sulphates, like **gypsum** $CaSO_4,2H_2O$, **barite** $BaSO_4$, and **celestite** $SrSO_4$, are fairly plentiful. The deposits of free sulphur are believed to have been formed mainly from gypsum, by reduction. Sulphur is a constituent of the proteins, which are important components of the structures of plants and of animals.

Manufacture. — In Sicily sulphur is obtained by the simple process of melting it away from the accompanying volcanic rock at a low temperature. A part of the sulphur itself is burned, to

obtain heat to melt the rest, because no coal is found in Italy, and fuels other than sulphur are locally too expensive. The liquid sulphur is allowed to run into wooden molds, in which it solidifies in the form of **roll sulphur,** or **brimstone.** For many purposes this

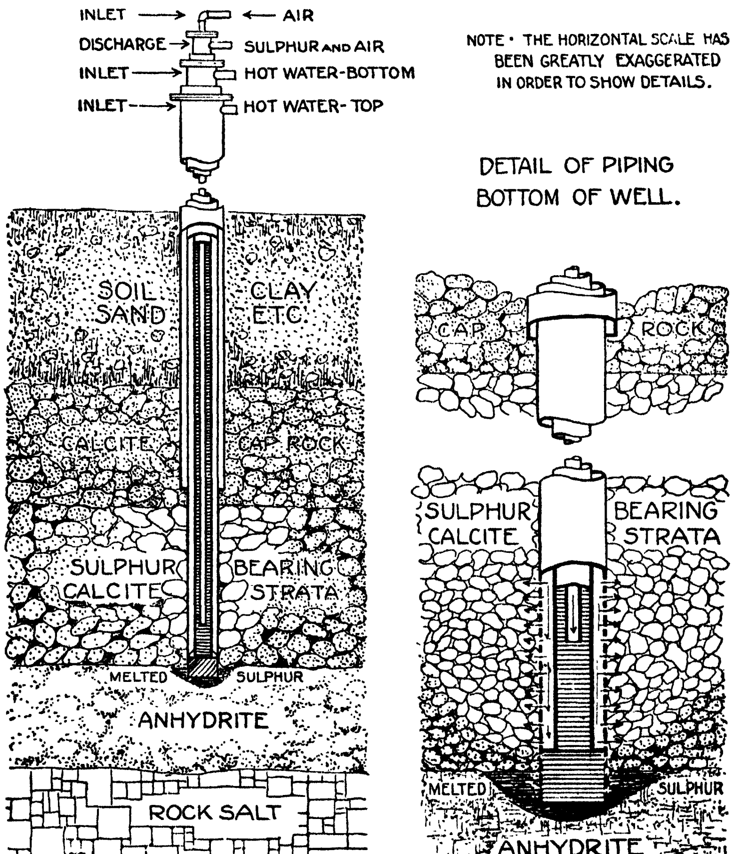


FIG. 120. Frasch Process for Extracting Sulphur.

sulphur is sufficiently pure. To produce the best quality it is subjected to distillation from earthenware retorts. The vapor passes into a large brick chamber and condenses upon the walls and floor in the form of a fine powder, sold as **flowers of sulphur.** When the chamber has become heated, the sulphur condenses in the form of a liquid, which is drawn off and cast in molds as before.

In Texas and Louisiana, the sulphur occurs in the cap-rock overlying certain salt domes, below 900 feet of clay, quicksand, and rock. It is extracted by the **Frasch method,** by means of borings which permit four pipes, one within the other, to reach the deposit. Water, previously heated under pressure to 170°, is pumped down the two outside pipes (6 and 8 inches in diameter). After time has been allowed for the melting of a quantity of the sulphur (it melts at 114.5°), compressed air is pumped down through an inner, one-inch pipe. The melted sulphur, alone, has twice the specific gravity of the water in the outer pipes. But the air breaks up into small bubbles, forming with the liquid sulphur an emulsion which has a lower specific gravity, and this flows freely up a three-inch pipe

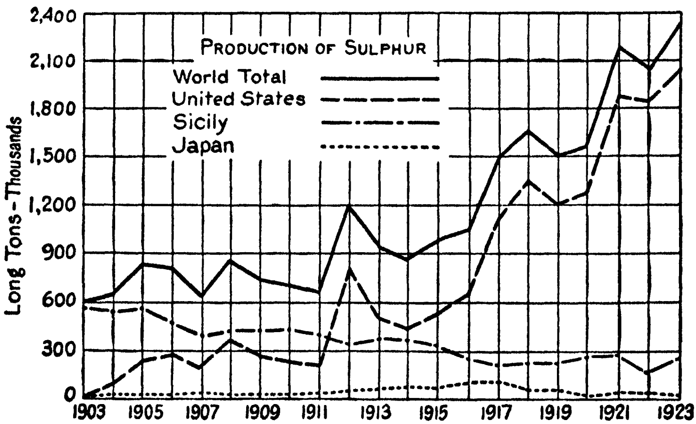


FIG. 121. Effect of the Frasch Process on Sulphur Production.

which surrounds the air pipe (see Fig. 120). The sulphur runs into wooden enclosures, measuring 150 by 250 feet, in which it quickly solidifies. The product is so pure that, for most purposes, no other treatment is required.

The greater part of the sulphur of commerce formerly came from Sicily, but the development of the deposits in the Gulf States by the Frasch process has exercised a very adverse effect upon the older and cruder industry. This is clearly shown in Fig. 121, which charts the data for the years 1903–23. Since 1923 both domestic and foreign productions have been most erratic, due to business fluctuations, but the 1935 figures — 1,633,000 tons for the United States and 365,000 tons for Italy — indicate that conditions are now practically back to the 1923 basis.

Some sulphur is obtained in the purification of illuminating gas. The sulphur compounds present in the gas (mainly hydrogen sulphide), are a source of annoyance, both because of their tarnishing action on metals and because of the formation of sulphur dioxide on burning. Their removal is now effected by introducing into the gas a restricted quantity of air, sufficient only to supply the oxygen necessary for the reaction:

$$2H_2S + O_2 \rightarrow 2H_2O + 2S.$$

This action is induced to take place by passing the gas at 300° over bog iron ore (hydrated ferric oxide ignited at a low temperature), which functions as a catalyst. The hot gases are subsequently passed into a series of condensing chambers, where the sulphur separates.

Locally, the alkali waste (black ash) of the LeBlanc soda process (p. 714) is also employed as a source of sulphur. The calcium sulphide contained therein is decomposed by means of carbon dioxide:

$$CaS + H_2O + CO_2 \rightarrow CaCO_3 + H_2S$$

and the hydrogen sulphide converted to sulphur by the same process as outlined above.

Allotropic Forms of Sulphur. — Sulphur appears in two different liquid forms, and in several perfectly distinct solid varieties. The two most familiar forms of the latter are called, from their crystalline habits, **rhombic** and **monoclinic** sulphur.

Rhombic Sulphur. — This, the more common crystalline variety, is yellow, with *specific gravity* 2.06. Specimens of natural sulphur often show the rhombic form very clearly. All the forms of sulphur are *insoluble* in water, and all the crystalline forms are *soluble* in carbon disulphide. Good rhombic crystals are obtained from the solution (Fig. 7, p. 20).

The rhombic form is stable when not heated above 96°. If kept above this temperature, it changes into monoclinic sulphur.

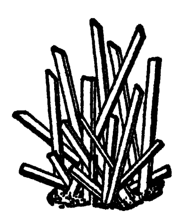


FIG. 121a. Monoclinic Sulphur.

Monoclinic Sulphur. — This form is obtained most readily by first melting some sulphur (m.-p. 114.5°), and then allowing it slowly to cool. As the temperature is now above 96°, the crystals which grow in the liquid are of the monoclinic variety. They are long, transparent, pale-yellow needles (Fig. 121a), almost rectangular in section and beveled at the points. The specific gravity is 1.96. This form can be kept indefinitely above 96°, but below that temperature the mass gradually becomes opaque, the change usually spreading from the points at

which it has been touched and finally affecting the whole mass. The opacity is due to the fact that the material has turned into an aggregate of small particles of rhombic sulphur, each of which occupies less space than the monoclinic sulphur from which it was formed. Conversely, when rhombic sulphur is heated above 96°, but not as high as its melting-point, contact with a piece of monoclinic sulphur, or mere rubbing with a hard body, will determine the point at which the transformation shall begin, and the expansion which accompanies this results in a spreading opacity as before. The delay before the change starts and the effect of rubbing and inoculation are familiar in connection with almost all changes of state (compare p. 207).

Transitions, marked by definite points, like this one at 96°, are attended by similar phenomena, whether they lie between two solid states, or a liquid and a solid state (ice and water), or a gaseous and a liquid state (steam and water). Heat is given out when we pass in one direction and absorbed when we pass in the other. Only at the definite **transition point** (p. 164) can any two crystalline forms exist together in equilibrium.

The Two Liquid Forms: Amorphous Sulphur. — When sulphur is melted, and the liquid is heated, two fluid, mutually soluble forms of sulphur are produced. These are known as S_λ and S_μ. As the temperature rises, the second variety increases in quantity at the expense of the first. When the temperature is lowered, the reverse change occurs. The equilibrium proportion of S_μ varies from 3.6 per cent at 120° to 11 per cent at 160° and about 34 per cent at 445° (the boiling-point of sulphur). S_μ is very viscous, so that, as its quantity increases, the whole liquid becomes thick. At 120° molten sulphur is a pale-yellow, limpid fluid; at 260° a vessel containing it can be inverted for a considerable time without loss of the dark-brown viscous material.

If the temperature of molten sulphur is lowered gradually, therefore, only monoclinic sulphur (by crystallization of the S_λ) is obtained, the reversible reaction $S_\lambda \rightleftarrows S_\mu$ proceeding to completion in the backward direction owing to the removal of S_λ (compare p. 282). But the change from S_μ to S_λ takes place only very slowly, except at temperatures near the boiling-point. Consequently, if the liquid is quickly chilled, by pouring into a cold vessel or into cold water, the S_μ persists as a non-crystalline substance mixed with more or less crystallized S_λ. The whole of the S_λ can be dissolved out with carbon disulphide, leaving the **amorphous sulphur, which is not soluble.**

Amorphous sulphur is a *supercooled liquid,* and not a true solid, for true solids are all crystalline (see pp. 59–62). At room temperature it changes into rhombic sulphur, but so very slowly that the transformation even of a small part of it can be detected (by treating with carbon disulphide) only after the lapse of many months. At 100° the change is complete in less than an hour (compare p. 99).

Much original work on the allotropic forms of sulphur was done by Alexander Smith himself, while at the University of Chicago. Among many other interesting points, he discovered that the attainment of equilibrium between the two liquid forms of sulphur could be accelerated or delayed by the introduction of small traces of impurities. Ammonia acts as a *positive catalyst,* iodine or sulphuric acid as a *negative catalyst.* When dry ammonia gas is bubbled through the viscous melt, the transformations that occur after this is chilled take place quite rapidly, and the product very soon becomes opaque and hard. With a trace of iodine present, on the other hand, the chilled material remains in a sticky plastic state for several days. Under the ordinary conditions of heating the element in an open test-tube, a sufficient amount of sulphuric acid is usually formed by oxidation of the surface sulphur in moist air (see p. 402) to make the **elastic** or **plastic sulphur** obtained by rapid cooling fairly persistent.

Recent work upon sulphur shows that conditions are even more complex than was postulated by Professor Smith. Besides mother-of-pearl sulphur, a third crystalline variety, we have to recognize at least two new liquid forms, S_π and S_ρ.

Melting-Points and Freezing-Points. — Amorphous sulphur, like glass and other amorphous substances, softens when heated, but has no sharp melting temperature. The two crystalline forms have different melting-points, rhombic melting to form S_λ at 112.8°, and monoclinic melting at 119.25°. But these two points are difficult to obtain, as the rhombic tends to turn into monoclinic above 96°, and gradual transformation of S_λ to S_μ to produce an equilibrium mixture of the two with a lower freezing-point than that of pure S_λ, occurs in both cases in the liquid state. Hence, the only true equilibrium temperature which is easy to observe is that at which the liquid freezes if cooled *exceedingly slowly,* namely 114.5°. This is the so-called *natural freezing-point* of sulphur.

Chemical Properties. — The vapor density of sulphur indicates that the vapor is a mixture of the molecules S_8, S_6 and S_2, the former diminishing and the latter increasing in number as the temperature is raised (see p. 194).

All the *metals,* excepting gold and platinum, *combine* with sulphur to form sulphides, and in most cases much heat is given out

during the union. Sulphur unites with *chlorine* to give sulphur monochloride S_2Cl_2, used in vulcanizing rubber, and burns in *oxygen* to give sulphur dioxide: *

$$S + O_2 \rightarrow SO_2.$$

When sulphur is treated with oxidizing agents *in presence of water,* no trace of sulphur dioxide (or sulphurous acid) is formed; the only product is sulphuric acid (see p. 424). Even the oxygen in the air slowly oxidizes sulphur, with the help of atmospheric moisture, to give sulphuric acid:

$$2S + 2H_2O + 3O_2 — 2H_2SO_4.$$

In the above equations, it will be noted, the simple formula S is used in place of a molecular formula. The latter is needed only when questions about the volume of the vapor are asked, and sulphur is almost always used only in solid or melted form. Then, too, the vapor contains several kinds of molecules, and using S_8 or S_6 would introduce large and inconvenient coefficients.

In combination with metals and hydrogen, sulphur is bivalent, forming compounds like H_2S, FeS, CuS, and HgS. In combination with non-metals, however, the valence is frequently greater, the maximum being seen in sulphur trioxide, where we must assume that the sulphur is sexivalent. Its oxides are acid-forming, and it is, therefore, a non-metal.

Hydrogen Sulphide H_2S

This gas is found dissolved in some mineral waters, which in consequence are known as sulphur waters. It is produced in the decomposition of animal matter containing sulphur (proteins), when air is excluded. Hence the odor of rotten eggs is due in part to its presence.

Preparation. — Hydrogen and sulphur do not unite perceptibly in the cold. At 310° almost complete union occurs, but about seven days are required for the attainment of equilibrium.

Sulphides of metals, being salts, are acted upon more or less easily by dilute acids, and give hydrogen sulphide. Ferrous sulphide, the least expensive of those easily affected, is generally used:

$$FeS + 2HCl \leftrightarrows H_2S \uparrow + FeCl_2.$$

* Traces of sulphur trioxide are found at the same time. They give minute drops of sulphuric acid, which cause a haziness in the gas when it is formed by this action.

The action, like all double decompositions, is reversible. But use of an excess of hydrochloric acid forces it forwards, and the escape of the gaseous hydrogen sulphide reduces the backward action almost to zero. The gas can be made in a flask fitted like that in Fig. 64 (p. 132), or in a Kipp's automatic generator (Fig. 65, p. 133). It can be collected by upward displacement.

Hydrogen sulphide is the invariable product of the extreme reduction of any sulphur compound. Thus, it is formed by the action of hydrogen iodide, or of zinc, upon concentrated sulphuric acid (pp. 352, 133). Even sulphur itself is reduced by dry, gaseous hydrogen iodide (compare p. 353):

$$2HI + S \rightarrow H_2S + I_2.$$

Physical Properties. — Hydrogen sulphide is a *colorless* gas with an *odor* recalling rotten eggs. It is rather easily *liquefied,* and the liquid boils at —61.6° and freezes at —82.9°. The formula H_2S shows that the gram-molecular volume weighs 34 g., so that the density is about one-sixth greater than that of air. The gas is moderately soluble in water (290 vols. in 100 vols. water at 20°), a property which enables us to carry out many reactions of the gas upon substances in solution. Its critical temperature, under a pressure of 89 atmospheres, is 100°.

Hydrogen sulphide is poisonous, so that care must be taken to allow as little of the gas as possible to escape into the air, and all work with it should be done in a well-ventilated hood. The proportion must reach 1 part in 200 of air, however, before fatal results follow breathing the mixture. The best antidote is very dilute chlorine.

Chemical Properties. — 1. The gas *burns* in the air, giving water and sulphur dioxide:

$$2H_2S + 3O_2 \rightarrow 2H_2O + 2SO_2.$$

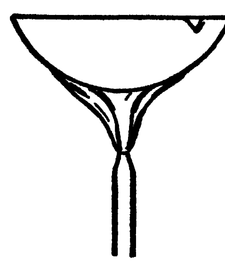


FIG. 122. Partial Combustion of Hydrogen Sulphide.

2. The compound is *not very stable.* When heated, for example, in the interior of its own flame, it is partially decomposed into free sulphur and hydrogen. A cold porcelain dish (Fig. 122) placed in the flame will condense some of the sulphur on its surface and a part of the hydrogen is also liable to escape unburnt. It may be remarked that dissociation of this kind probably precedes the combustion of most gaseous compounds (see Flame).

Sulphur is deposited also when hydrogen sulphide undergoes a partial combustion with a restricted supply of oxygen (see p. 399).

3. On account of its instability, and the ease with which it gives up hydrogen, the gas is a *reducing agent*. Thus, when jars of hydrogen sulphide and sulphur dioxide are placed mouth to mouth, a deposit of sulphur gradually appears:

$$SO_2 + 2H_2S \rightarrow 2H_2O + 3S.$$

Part of the free sulphur found in nature seems to be liberated by the action of these gases, both of which are found in volcanic regions. The gases must be moist, for, without water vapor as a catalyst, no appreciable interaction occurs.

When hydrogen sulphide gas is led through concentrated, or even, simply, normal sulphuric acid, the acid is reduced, sulphur dioxide escapes, and sulphur is deposited:

$$H_2S + H_2SO_4 \rightarrow S + 2H_2O + SO_2.$$

On account of this action the gas cannot be dried by means of concentrated sulphuric acid. Calcium chloride is likewise inapplicable, since a partial interchange takes place, resulting in the production of calcium sulphide and hydrogen chloride gas. Only a dehydrating agent such as phosphoric anhydride, with which it cannot interact, is suitable for drying the gas.

4. The metals, down to and including silver in the activity series, quickly receive a coating of sulphide when exposed to the gas:

$$2Ag + H_2S \rightarrow Ag_2S + H_2 \uparrow.$$

The tarnishing of silver in the household is due to the presence of a trace of hydrogen sulphide in the illuminating gas which escapes from slight leaks in the pipes.

Chemical Properties of the Aqueous Solution of Hydrogen Sulphide. — While the gas itself is not an acid, its solution in water gives a **feeble acid reaction** with litmus, and is sometimes named **hydrosulphuric acid.** The conductivity of a $N/10$ aqueous solution is small, and only 0.0007 (0.07 per cent) of the substance is ionized:

$$H_2S \rightleftarrows H^+ + HS^- \ (\rightleftarrows H^+ + S^=).$$

The second dissociation of the small amount of hydrosulphide-ion HS^- into H^+ and $S^=$ is almost negligible, and the amount of sulphide-ion $S^=$ present is therefore exceedingly minute.

As an acid, the solution of hydrogen sulphide may be neutralized by bases. For the same reason it enters into double decomposition with salts, giving insoluble sulphides (see p. 411).

By the action of **oxygen** from the air upon an aqueous solution of hydrogen sulphide, the **sulphur** is slowly **displaced** and appears in the form of a fine white powder:

$$O_2 + 2H_2S \rightarrow 2S\downarrow + 2H_2O.$$

This is an action similar to the displacement of ionic bromine by free chlorine (p. 359).

The solution of the gas is a **reducing agent,** as its action upon iodine shows (p. 352). So, also, in presence of an acid, it removes oxygen from potassium dichromate:

$$K_2Cr_2O_7 + 8HCl + 3H_2S \rightarrow 2KCl + 2CrCl_3 + 7H_2O + 3S.$$

This is another good equation for the student to exercise his ingenuity upon, using the methods described in pp. 378–9 to balance it correctly.

Dibasic Acids. — Acids containing two ionizable atoms of hydrogen in each molecule are called **dibasic acids.** H_2CO_3 (p. 566), H_2S, H_2SO_3 and H_2SO_4 are such acids. Each molecule is able to react with two molecules of a base like sodium hydroxide, as may be seen in the succeeding section. When half the quantity of the base is used, an *acid salt* (p. 291) is produced. Phosphoric acid H_3PO_4 is a **tribasic** acid, and forms two series of acid salts, for example NaH_2PO_4 and Na_2HPO_4. Hydrochloric acid HCl and nitric acid HNO_3 are **monobasic.**

Sulphides. — As a dibasic acid, hydrogen sulphide gives both acid and normal (or "neutral") sulphides, such as NaHS and Na_2S. The names *acid* and *neutral,* as we shall see, refer here to the *constitution* of the compounds (see p. 291), **not** to the behavior of their solutions.

The **acid sulphides** (hydrosulphides) are obtained by passing the gas *in excess* into solutions of soluble bases:

$$H_2S + NaOH \rightleftarrows H_2O + NaHS.$$

By adding to the above-mentioned solution of sodium acid sulphide (which reacts **very faintly alkaline** to litmus), an amount of sodium hydroxide equal to that used before, and driving off the water by evaporation, the second unit of hydrogen is displaced, and **normal** ("neutral") **sodium sulphide** is formed:

$$NaOH + NaHS \rightarrow Na_2S + H_2O \uparrow .$$

The solution of this salt in water is **strongly alkaline** in reaction. **In general, any normal salt derived from a strong base and a weak acid** gives an **alkaline solution.** The explanation by the ionization theory is thus of general interest.

Water, it will be remembered, is ionized to a very small extent. When *any salt* RX is dissolved in water, therefore, there exists the *possibility* of a double decomposition taking place. On the basis of the modern theory that practically all salts are completely ionized, while the ionization of acids and bases may be only partial, we may formulate the general equilibrium as follows:

$$\begin{array}{rcccc} & & R^+ & + & X^- \\ H_2O & \rightleftarrows & OH^- & + & H^+ \\ \hdashline & & \uparrow\downarrow & & \uparrow\downarrow \\ & & ROH & & HX \end{array}$$

In many cases, however, the extent of formation of ROH and HX is altogether negligible. For example, in the case of NaCl, since NaOH and HCl are both completely ionized in aqueous solution, the equilibria below the dotted line in the above formulation drop out entirely, and the ionization of the solvent is absolutely unaffected by the addition of the salt. All solutions of salts derived from a strong acid and a strong base, indeed, are **neutral** in fact as well as in name.

When a salt like sodium sulphide is dissolved in water, the state of affairs is different, as may be seen by studying the arrows in the ionic equations:

$$\begin{array}{rcccc} & & 2Na^+ & + & S^= \\ 2H_2O & \rightleftarrows & 2OH^- & + & 2H^+ \\ & & & & \uparrow\downarrow \\ & & & & H_2S \end{array}$$

Double decomposition with the ions of water here involves the formation of undissociated H_2S, since this substance is an *exceed-*

ingly weak acid. A certain amount of hydrogen-ion will thus be withdrawn from the solution, disturbing the equilibrium $H_2O \rightleftarrows H^+ + OH^-$. In order to re-establish this equilibrium, more H_2O will ionize, but while all of the hydroxyl-ion thus formed remains as such in the solution, most of the hydrogen-ion again disappears in the reaction $2H^+ + S^= \rightleftarrows H_2S$. The large concentration of $S^=$ present in the solution acts as a powerful additional stimulant for this annihilation of H^+ (see p. 270). In the presence of a large excess of sulphide-ion, indeed, H_2S will be practically non-ionized. Now we have learned (p. 334) that one way of driving a reversible reaction to completion is to remove one product *as a non-ionized substance.* This reaction cannot be driven *to completion* by formation of H_2S in this way, since we have the formation of another practically non-ionized substance, water, tending to drive the reverse reaction to completion. In such circumstances, obviously, a balance must be struck between the two conflicting tendencies, and we shall be left with a solution in which *partial* double decomposition has occurred. But such a solution will contain a much higher concentration of OH^- than of H^+. It will, therefore, react like an **alkali.**

Properties of Sodium Hydrosulphide Solution. — The faint alkalinity of a solution of this salt in water may also be understood by reference to the formulation given below.

$$\begin{array}{rl:l} & Na^+ + HS^- & \rightleftarrows H^+ + S^= \\ H_2O \rightleftarrows & OH^- + H^+ & \\ & \qquad\ \ \upharpoonleft\downharpoonright & \\ & \qquad\ \ H_2S & \end{array}$$

Restricting our attention at first to the equilibria represented to the *left* of the dotted line, we see that, just as in the preceding case of sodium sulphide, any double decomposition with the ions of water will result in the solution becoming alkaline. But there is here another factor to be taken into account. The anion HS^- of sodium hydrosulphide, as we have seen above (p. 404), possess a tendency, albeit extremely slight, to dissociate again into H^+ and $S^=$. If this tendency were at all pronounced, a solution of sodium hydrosulphide would necessarily react *as an acid,* owing to the H^+ produced. It would be, in fact, true to its name, an *acid salt.* But here *the amount of* H^+ *resulting from the dissociation of* HS^- is *so small that it does not quite equal the excess of* OH^- *result-*

from the double decomposition between NaHS *and* H_2O. There is therefore still a slightly greater concentration of OH^- than of H^+ in the solution, and the solution consequently reacts very faintly alkaline.

It may be noted at this stage that the formulation given in the case of sodium sulphide above (p. 406) is not *strictly* accurate, since in the last vertical column a direct equilibrium between the ions $2H^+$ and $S^=$ and the undissociated molecule H_2S is postulated, whereas in point of fact combination of the ions takes place in two stages through the intermediate ion HS^-. The student will discover, nevertheless, if he formulates the action for himself in the two stages, that the same conclusion is thereby reached, and within the scope of this volume we shall find the abbreviated method of formulation employed on p. 406 not only sufficient for the present illustration, but also exceedingly useful in explaining many similar reactions in analytical chemistry which will come up for discussion later.

Hydrolysis of Salts. — The interaction of a salt with water is called **hydrolysis.** The action is the reverse of neutralization (p. 332), water and salt giving, by double decomposition, an acid and a base. *The effect is noticeable,* however, only *when the acid and base are of very unequal activity.* **A salt which, by hydrolysis, gives a strong base and a weak acid, furnishes a solution the reaction of which is basic.** Thus the solution of sodium carbonate in water reacts basic, because carbonic acid is a feeble acid.

Conversely, **if the salt gives, by hydrolysis, a weak base and a strong acid, then the solution is acid in reaction.** Thus, the solution of cupric sulphate reacts acidic because cupric hydroxide is a feeble base.

The extent of hydrolysis, even in cases where it is distinctly observable, such as sodium carbonate and cupric sulphate mentioned above, is in general only small. Borax, a salt of an extremely weak acid (p. 317), reacts distinctly alkaline in water, but the degree of hydrolysis in a 0.1 *N* solution at 25° is only one-half of one per cent. The reason, of course, lies in the fact that water is very much less ionized even than most exceedingly weak acids like boric acid or most exceedingly weak bases like cupric hydroxide. The tendency towards the completion of *neutralization,* therefore, preponderates considerably in most cases over the tendency towards the completion of *hydrolysis.* Other things being equal, salts containing bivalent or trivalent radicals are more noticeably hydrolyzed than are those composed only of univalent radicals.

When we consider a salt of an *extraordinarily* weak acid or base, nevertheless, very extensive hydrolysis in solution must evidently occur. An ex-

ample is immediately available in the case of sodium sulphide. The tendency towards the second stage of ionization in H_2S, as expressed by the equation $HS^- \rightleftarrows H^+ + S^=$, is exceedingly slight. In other words, as a *dibasic acid* hydrosulphuric acid is *exceedingly weak*. It is, indeed, *even weaker than water*. In consequence of this, the degree of hydrolysis in a solution of "neutral" sodium sulphide is very high, and the solution reacts strongly alkaline. As a matter of fact, if we formulate the hydrolysis in strict detail in two stages, as suggested above, and consider the various equilibria quantitatively, we find that a decinormal solution of sodium sulphide in water at 25° is hydrolyzed to the extent of 86.4 per cent into sodium hydrosulphide and sodium hydroxide. The hydrolysis of sodium hydrosulphide, on the other hand, is relatively inappreciable. As a *monobasic acid,* hydrosulphuric acid, though ordinarily classed as a "weak" acid, is *enormously stronger than water,* and we find accordingly that the degree of hydrolysis of a decinormal solution of sodium hydrosulphide in water at 25° is only 0.14 per cent.

It should be noted that substances such as phosphorus tribromide (p. 346), silicon tetrachloride (p. 659) and other compounds of purely non-metallic elements are **completely** hydrolyzed by water. These substances are **not** salts, and ionic equilibria are **not** involved in their decomposition.

The Action of Acids on Insoluble Sulphides. — The interaction of sulphides and acids is itself so important a matter in chemistry, and is so similar in theory to many other kinds of actions, that some attention must be given to it here, although the *quantitative* discussion of the various points involved will be more appropriately taken up in a later chapter (pp. 760–3). The common method of preparing hydrogen sulphide by the action of hydrochloric acid on ferrous sulphide (p. 402) affords a suitable illustration.

Since ferrous sulphide is but slightly soluble in water, and may be regarded as completely ionized in aqueous solution, the action proceeds by the following series of equilibria:

$$FeS\text{ (solid)} \rightleftarrows \left.\begin{matrix} Fe^{++} + S^{=} \\ 2Cl^- + 2H^+ \end{matrix}\right\} \rightleftarrows H_2S\text{ (dissolved)} \rightleftarrows H_2S\text{ (gas)}.$$

It will be seen that a number of reversible changes are involved, and the question is, why does the reaction proceed forward, as it does? To answer this question, a consideration of each of the equilibria, separately, is required.

1. The dissolved hydrogen sulphide is very feebly ionized, and maintains a smaller concentration of sulphide-ion $S^=$ than does ferrous sulphide, in spite of the comparative insolubility of the latter. Hence, the $S^=$ formed from the FeS is continuously being removed by union with the hydrogen-ion furnished by the acid, and all the other equilibria are constantly displaced forward on

this account. The action is therefore, in essence, like neutralization (p. 332).

2. The extent to which the union of sulphide-ion and hydrogen-ions approaches completeness depends on the magnitude of the *product* of their concentrations (p. 273). Here, although $[S^=]$ is minute, on account of the very low solubility of FeS, $[H^+]$ is large on account of the complete dissociation of the HCl and the fact that a concentrated solution of the acid can be used. Thus the *product* is still large enough to carry the reaction forward.

3. The fact that hydrogen sulphide is fairly soluble in water *hinders* the progress of the action. It prevents that free escape of one product which is so constantly a factor in promoting reversible chemical changes. Here the retention of H_2S in the solution makes it impossible, finally, to maintain $[S^=]$ below a certain fixed concentration, dependent upon the particular concentration of hydrogen-ion H^+ present, and since, as the reaction proceeds, the concentration of ferrous-ion Fe^{++} also steadily increases, we are inevitably tending towards a point where the product of the concentrations of $S^=$ and of Fe^{++} will be such that no more FeS will dissolve. Indeed, if cadmium sulphide CdS, which is less soluble than ferrous sulphide, is treated with rather dilute hydrochloric acid, a concentration of hydrogen sulphide sufficient to stop the action accumulates even before the liquid is saturated with the gas.

4. There are then two ways of making this action continuous. Either more concentrated hydrochloric acid, giving a higher concentration of H^+, may be used to force the formation of more H_2S (by union of $2H^+$ and $S^=$), or the reverse action, due to accumulation of H_2S (dissolved), may be diminished mechanically by leading air through the mixture (p. 219) and so removing the hydrogen sulphide as fast as it is formed. Either plan will cause complete interaction with the cadmium sulphide.

5. When a still more insoluble sulphide, like mercuric sulphide HgS is employed, a concentration of H^+ sufficient to reduce the concentration of $S^=$ in the solution below the limiting value cannot be obtained *with any acid.* The reaction therefore automatically comes to a stop almost as soon as it begins.

Classification of Insoluble Sulphides. — In analytical chemistry, advantage is taken of the different solubilities of the sulphides, for the purpose of identifying the metallic elements, and of sepa-

rating mixtures containing several such elements. Three classes are distinguished.

1. The sulphides of silver, copper, mercury, and some other metals are exceedingly insoluble, and, therefore, do not interact at all with dilute acids. In fact, they may very readily be made by leading hydrogen sulphide into solutions of their salts:

$$CuSO_4 + H_2S \leftrightarrows CuS \downarrow + H_2SO_4.$$

The acid produced has scarcely any effect upon the sulphide, and almost no reverse action is observed. In this action the sulphide-ion is the active substance and, by its removal, all the equilibria are displaced forwards. The precipitation of black PbS from a solution of lead acetate is used as a *test* for hydrogen sulphide.

2. The sulphides of iron, zinc, and certain other metals are insoluble in water, but not so much so as the last class. Hence they are decomposed by dilute acids, and the reverse of the above action takes place almost completely. These sulphides must therefore be made, either by combination of the elements, or by adding a soluble sulphide (which furnishes a greater concentration of $S^{=}$ than H_2S does) to a solution of a salt:

$$FeSO_4 + (NH_4)_2S \leftrightarrows FeS \downarrow + (NH_4)_2SO_4.$$

No acid is produced in this sort of interaction, and the very minute solubility of the sulphide of iron or zinc in water renders the change nearly complete.

3. The sulphides of barium, calcium, and some other metals, although insoluble in water as such, are hydrolyzed by it, and give soluble products, the hydroxide and hydrosulphide:

$$2CaS + 2H_2O \leftrightarrows Ca(OH)_2 + Ca(SH)_2.$$

They may be prepared by direct union of the elements, and from the sulphates by reduction with carbon. But they are **not** precipitated by hydrogen sulphide or ammonium sulphide.

Polysulphides. — When sulphur is shaken with a solution of a soluble sulphide, such as sodium sulphide, it dissolves, and evaporation of the solution leaves residues, varying in composition from Na_2S_2 to Na_2S_5. These appear to be mixtures of Na_2S and various **polysulphides,** of which Na_2S_2 and Na_2S_4 are the most stable.

When an acid is poured into sodium polysulphide solution, minute spherules of rhombic sulphur are precipitated:

$$Na_2S_4 + 2HCl \rightarrow 2NaCl + H_2S \uparrow + 3S \downarrow.$$

This precipitate has been called "soluble amorphous sulphur." It is certainly all soluble in carbon disulphide, but the particles rotate the plane of polarization of polarized light (A. Smith), and are therefore not truly amorphous, but composed of exceedingly minute crystals (compare **amorphous charcoal,** p. 561). Insoluble, **truly** amorphous sulphur, in appreciable quantities, cannot be obtained under any conditions from polysulphides. It is obtained, however, by adding sodium thiosulphate solution (p. 431) to concentrated, active acids.

When the order is reversed, sodium pentasulphide being thrown into concentrated hydrochloric acid, no hydrogen sulphide is evolved. **Hydrogen pentasulphide,** H_2S_5, a yellow oil, falls to the bottom of the vessel.

The soluble acid sulphides are **oxidized** in aqueous solution by atmospheric oxygen:

$$2NaSH + O_2 \rightarrow 2NaOH + 2S.$$

The sulphur is not precipitated, but combines with the excess of the sulphide, forming polysulphides. Some sodium thiosulphate is produced at the same time.

The Chemical Relations of the Element. — In combination with metals and hydrogen, sulphur is bivalent, forming compounds like H_2S, FeS, CuS, and HgS. In combination with non-metals, however, the valence is frequently greater, the maximum being seen in sulphur trioxide, where we must assume that the sulphur is sexivalent. Its oxides are acid-forming, and it is, therefore, a non-metal.

Sulphur is regarded as resembling oxygen more closely than any of the other elements *we have studied so far.* Both unite directly with most metals and non-metals. In this they are like chlorine. But hydrogen chloride is highly ionized by water, while the hydrogen compounds of oxygen and sulphur are feebly ionized. The formulæ of the compounds of oxygen and sulphur with metals are similar, CuO and CuS, NaOH and NaSH, and so forth, but this is in part due merely to the fact that both elements are bivalent. The chemical resemblance of sulphur to selenium and tellurium (p. 437) is much more striking than its resemblance to oxygen.

Exercises. — 1. How could the decomposition of hydrogen sulphide at 310° be rendered, (*a*) more complete, (*b*) less complete? Would the percentage decomposed be affected, (*a*) by reducing the pressure, (*b*) by mixing the gas with an indifferent gas?

2. What are the relative volumes of the gases (p. 250) in the action of (*a*) hydrogen iodide and sulphur, (*b*) hydrogen sulphide and sulphur dioxide?

3. Formulate completely, after the model on p. 409, the actions of (*a*) hydrogen sulphide and cupric sulphate solution; (*b*) ammonium sulphide and ferrous sulphate. In each case explain which equilibrium determines the direction of the action.

4. Is heat evolved, or absorbed, when monoclinic sulphur changes over to rhombic sulphur? Is heat evolved, or absorbed, when S_λ changes over to S_μ? Apply Van't Hoff's Law (p. 284).

5. Would equal weights of rhombic and monoclinic sulphur give out equal or different amounts of heat on burning? If different, which would give more and which less?

6. Why is chlorine an antidote for hydrogen sulphide poisoning (see p. 359)?

7. Why does a solution of sodium sulphide in water tend to deposit sulphur on standing in contact with air?

8. Apply each of the two methods (pp. 378–9) of writing complex equations to balance the following skeleton reactions:

(*a*) $K_2Cr_2O_7 + HCl + H_2S \rightarrow KCl + CrCl_3 + H_2O + S$.
(*b*) $KMnO_4 + HCl + H_2S \rightarrow KCl + MnCl_2 + H_2O + S$.

9. A 5-liter cylinder containing sulphur dioxide is brought mouth to mouth with a 10-liter cylinder containing hydrogen sulphide, and the intervening plate removed. The experiment is performed in triplicate: (*a*) with the H_2S cylinder uppermost, (*b*) with the SO_2 cylinder uppermost, and (*c*) with the gases carefully dried in advance. What differences do you observe in the speed of the reaction in the three cases? Explain fully.

10. What difference is observed between the actions of dilute and concentrated hydrochloric acid upon ferrous sulphide, and to what is this difference due?

11. Will solutions of the following salts in water give an acid, a neutral, or an alkaline reaction: (*a*) sodium acetate, (*b*) potassium fluoride, (*c*) potassium-hydrogen fluoride KHF_2, (*d*) ammonium chloride? Formulate the equilibrium in detail in each case, and use the table on p. 317.

12. In what respects is sulphur similar, in its chemical relations, to oxygen? In what respects does it differ?

13. In what respects is sulphur similar, in its chemical relations, to chlorine? In what respects does it differ?

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CHAPTER XXIV

OXIDES AND OXYGEN ACIDS OF SULPHUR

There are two familiar oxides, namely, sulphur dioxide or sulphurous anhydride SO_2, and sulphur trioxide or sulphuric anhydride SO_3. Each of these dissolves in water and combines with it to form an acid. The former gives sulphurous acid H_2SO_3, and the latter sulphuric acid H_2SO_4.

Sulphur monoxide SO has recently been prepared by the action of an electric discharge on a mixture of sulphur dioxide and sulphur vapor at a low pressure. It is a gas, stable at ordinary temperatures, but decomposing into S and SO_2 when heated.

The oxides S_2O_3, S_2O_7 (or S_3O_{11} ?) and SO_4 are also known, but are of minor importance.

Sulphur Dioxide and Sulphurous Acid

Preparation of Sulphur Dioxide SO_2. — In *industrial practice* sulphur dioxide is obtained in three ways:

1. By burning sulphur (p. 95).
2. By burning natural sulphides, such as pyrite:

Skeleton: $FeS_2 + O_2 \rightarrow Fe_2O_3 + SO_2$.
Balanced: $4FeS_2 + 11O_2 \rightarrow 2Fe_2O_3 + 8SO_2$.

With fairly pure pyrite the combustion has only to be started, the heat evolved in the reaction being sufficient to offset loss of heat by radiation and to keep it going of its own accord. But with some sulphides, like zinc blende ZnS, which is used as a source of sulphur dioxide as well as of zinc, the air must be strongly heated throughout to maintain the combustion:

$$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2.$$

Forced combustion of an ore, like this, is called **roasting, or calcining,** and is the first stage towards obtaining the metal. The oxide is subsequently reduced by heating with coke.

3. By dropping concentrated sulphuric acid into red-hot iron retorts:

$$2H_2SO_4 \rightarrow 2H_2O + 2SO_2 + O_2.$$

The acid here is decomposed by the heat before it has any real opportunity to react with the metal, consequently the latter, apart from a surface oxidation, remains unchanged.

In the laboratory a steady stream of gas is easily obtained by dropping hydrochloric acid upon crystals of sodium-hydrogen sulphite (Fig. 64, p. 132):

$$NaHSO_3 + HCl \rightleftarrows NaCl + H_2SO_3, \quad (1)$$
$$H_2SO_3 \rightleftarrows H_2O + SO_2 \uparrow . \quad (2)$$

This method takes advantage of two facts: (*a*) that sulphurous acid is only slightly ionized in solution, which renders reaction (1) practically complete, especially in the presence of an *excess* of HCl (see p. 410), and (*b*) that sulphurous acid is unstable and decomposes (equation 2) when there is not a large excess of water present.

Sulphur dioxide can also be made by the reduction of concentrated sulphuric acid by copper at a high temperature:

$$2H_2SO_4 + Cu \rightarrow 2H_2O + SO_2 + CuSO_4.$$

Some easily oxidized non-metals, such as carbon and sulphur, act in the same way, $C + 2H_2SO_4 \rightarrow 2H_2O + 2SO_2 + CO_2$.

Properties. — Sulphur dioxide is a *colorless* gas possessing a penetrating and characteristic *odor*. The weight of the G.M.V. of the gas (64 g.) shows it to be more than *twice as heavy as air*. By means of a freezing mixture of ice and salt (Fig. 123), the gas is easily condensed in a **U**-tube to a transparent mobile *fluid*, which boils at —8° and freezes at —72°. The critical temperature is high, 156°. At 20°, the liquid gives a vapor pressure of only 3¼ atmospheres, so that the liquid is readily handled and sold in glass syphons or in sealed tin cans. The *solubility* of the gas in water is very pronounced, about 4000 volumes of the gas dissolving in 100 volumes of water at 20° and 760 mm. The solution is completely freed from the gas by boiling (contrast p. 228).

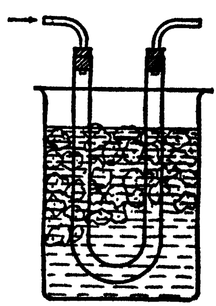


FIG. 123. Preparation of Liquid Sulphur Dioxide.

As regards **chemical properties,** sulphur dioxide is **stable** (p. 173). **It unites with water** to form sulphurous acid H_2SO_3, which is unstable and exists only in solution.

Since the maximum valence of sulphur is 6, sulphur dioxide, in which but four of the valences of sulphur are used, is **unsaturated** (see p. 151). It is therefore still able to combine directly with suitable elements, such as chlorine and oxygen. When it is mixed with chlorine in sunlight, **sulphuryl chloride** SO_2Cl_2 is produced.

Liquefied sulphur dioxide is employed for bleaching straw, wool, and silk (see p. 375). Enormous quantities of sulphur dioxide are employed in the manufacture of sulphuric acid and of sulphites.

The Liquefiabilities of Gases. — It will assist us in recalling which gases are hard to liquefy and which easy, if we memorize the fact that Faraday (from 1823 to 1845) liquefied most of the familiar gases and failed only with three, namely **hydrogen** (critical temperature —240°), **oxygen** (c.t. —118°), and **nitrogen** (c.t. —146°). These, with **nitric oxide** NO (c.t. —93.5°), **carbon monoxide** CO (c.t. —140°), **methane** CH_4 (c.t. —83°), and the six **inert gases** (p. 462), are the ones which have low critical temperatures (see p. 124) and are **difficult to liquefy.**

Of the gases we have studied, the ones which are more or less **easily liquefied** are: **hydrogen chloride** (c.t. +52°), **bromide,** and **iodide, chlorine** (c.t. +144°), **ozone, hydrogen sulphite** (c.t. +100°), **sulphur dioxide** (c.t. +156°).

The Solubilities of Gases. — For the purpose of remembering the solubilities of gases in water, it is convenient to divide the gases into **three classes.** The following are the ones we have studied:

1. **Slightly soluble: Oxygen** (4 vol. : 100 at 0°), **hydrogen** (2 : 100 at 0°).
2. **Soluble: Chlorine** (2.6 vol. : 1 at 10°), **hydrogen sulphide** (4.4 : 1 at 0°).
3. **Very soluble: Hydrogen chloride** (505 vol. : 1 at 0°), **bromide** (404 : 1) and **iodide** (1570 : 1), **sulphur dioxide** (69 : 1 at 0°).

Properties of Sulphurous Acid H_2SO_3. — Sulphurous acid, in aqueous solution, shows all the properties of a *transition acid* (p. 318). As already noted, concentrated solutions are very unstable. A solution of sulphurous acid therefore smells strongly of sulphur dioxide.

Being rather easily convertible into sulphuric acid H_2SO_4, sulphurous acid is a *reducing agent.* Thus oxygen from the air acts slowly upon the solution:

$$2H_2SO_3 + O_2 \rightarrow 2H_2SO_4$$

and iodine is turned into hydrogen iodide:

$$H_2SO_3 + H_2O + I_2 \rightleftarrows H_2SO_4 + 2HI.$$

In the particular case of iodine this action takes place only in very dilute solution, since concentrated sulphuric acid decomposes hydrogen iodide (p. 352) and the action is reversed. This interaction is

used in chemical analysis as a means of estimating the quantity of sulphurous acid in a liquid.

Hydrogen peroxide, potassium permanganate, and other oxidizing agents (for a detailed example, see p. 389) convert the substance into sulphuric acid likewise. It should be noted that in these oxidations we have, not an addition of oxygen to SO_2, but to the $SO_3^{=}$ or HSO_3^- ion of the acid, whereby it passes into the $SO_4^{=}$ or HSO_4^- ion of sulphuric acid. The ionic products are much more easily oxidized than is free sulphur dioxide itself.

When heated alone, in a sealed glass tube (150°), the acid reduces part of itself to sulphur, and a part is oxidized to sulphuric acid:

$$3H_2SO_3 \rightarrow 2H_2SO_4 + H_2O + S.$$

Sulphurous acid has the power of uniting directly with many organic coloring matters and, since the products of this union are usually colorless, it is employed as a **bleaching agent.** It is especially useful with chemically reactive materials like silk, wool, and fragile structures like straw, which are likely to be destroyed if bleaching powder is used. The compounds thus formed are unstable, and gradually lose the sulphurous acid again. Hence, wool yellows with age, and straw hats lose their whiteness. As a disinfectant sulphurous acid acts, perhaps, by addition likewise.

To prevent the growth of fungi or other organisms, wine casks are fumigated with sulphur dioxide before being filled. Dried peaches and apples are prepared by first exposing slices of the fruit on trays to sulphur dioxide. The sulphurous acid produced bleaches the fruit, keeps insects away, and prevents the formation of dark-colored substances during the subsequent drying.

Sulphites. — As a **dibasic acid,** sulphurous acid forms **normal salts** like Na_2SO_3, and **acid salts** like $NaHSO_3$. The **acid sulphites** (or **bisulphites,** compare p. 428) of the alkali metals, $KHSO_3$ and $NaHSO_3$, when in solution, are acid in reaction. Solutions of the **neutral sulphites,** however, react alkaline. Both series of salts are readily decomposed by strong acids to give free sulphurous acid, and the latter partly decomposes, yielding sulphur dioxide (p. 415).

Calcium bisulphite solution, $Ca(HSO_3)_2$, is used to dissolve the lignin out of wood, and leave the pure cellulose (paper pulp) employed in the manufacture of paper (see p. 600).

When **heated,** sulphites undergo decomposition. The sulphates, being the most stable of *all* the salts of sulphur acids, are formed when the salts of *any* of those acids are decomposed by heating. The nature of the particular salt determines what other product shall appear. Thus, with sodium sulphite Na_2SO_3, one molecule of the sulphite furnishes three atoms of oxygen, sufficient to oxidize

three other molecules, and leaves one molecule of sodium sulphide behind:

$$4Na_2SO_3 \rightarrow Na_2S + 3Na_2SO_4.$$

The acid sulphites (bisulphites) first lose sulphurous acid, before changing in this way. Thus, sodium-hydrogen sulphite begins by decomposing as follows:

$$2NaHSO_3 \rightarrow Na_2SO_3 + H_2SO_3 \ (\rightarrow H_2O + SO_2)$$

and at a higher temperature the sulphite Na_2SO_3 decomposes as explained above.

The acid salts of volatile acids, when heated, all decompose in this way (compare pp. 356, 715).

The sulphites are as readily **oxidized** as is the acid itself. They are slowly converted, both in solution and in the solid form, by the influence of the oxygen of the air, into sulphates. The rate of the reaction in solution is increased by addition of certain salts, copper sulphate having a noticeable effect even at a concentration as low as one-millionth of one-millionth normal! It is interesting to note that the addition of sugar or glycerine to a solution of a sulphite reduces the speed of oxidation by free oxygen very markedly. These substances act as catalysts; and the present case shows once more that agents of this kind do not always increase the speed of actions, though this is their usual function, but may instead have a restraining influence.

Sulphur Trioxide and Sulphuric Acid

Sulphur Trioxide. — Sulphur dioxide and oxygen, when heated together to 400°, unite very slowly with evolution of heat to give sulphur trioxide:

$$2SO_2 + O_2 \rightarrow 2SO_3 + 45{,}200 \text{ calories.}$$

This reaction, however, cannot be utilized for the manufacture of sulphur trioxide except under special conditions (see Contact process, p. 419), for at 400° the union ordinarily takes place far too slowly for use in industrial work, while at higher temperatures the reverse action becomes appreciable and poor yields are obtained. If we apply Van't Hoff's law to the reversible reaction: $2SO_2 + O_2 \rightleftarrows 2SO_3$ we see that, since the forward change is *exothermic*, raising the temperature will favor the backward change. In actual

practice it is found that at 400°, 98–99 per cent of the materials unite; at 700°, only 60 per cent; at 900°, practically none.

Formerly sulphur trioxide was obtained by the distillation of impure ferric sulphate, $Fe_2(SO_4)_3 \rightarrow Fe_2O_3 + 3SO_3$. It may also be prepared by repeated distillation of concentrated sulphuric acid with a still more powerful drying agent, like phosphoric anhydride.

Physical Properties. — Sulphur trioxide SO_3 is a white solid which exists in two allotropic crystalline forms. One melts at 17°, and is therefore fluid at ordinary temperatures. The liquid boils at 46°, and is, therefore, exceedingly volatile at room temperature. It fumes strongly when exposed to the air, in consequence of the union of the vapor with moisture and the production of minute drops of sulphuric acid.

A white crystalline variety of the substance, which in appearance closely resembles asbestos, is obtained when a trace of water has gained access to the fluid form. When heated to 50°, this passes into vapor of SO_3 without melting. This white solid is the more stable and more familiar form of the trioxide.

Chemical Properties. — The vapor of sulphur trioxide, when heated, **dissociates** into sulphur dioxide and oxygen (see above).

Sulphur trioxide is not itself an acid, but it is the **anhydride** of sulphuric acid. When placed in water it unites vigorously, causing a hissing noise due to the steam produced by the heat of the union.

Just as sulphur trioxide unites with water to give hydrogen sulphate, so it **combines** vigorously **with** many **oxides of metals,** producing the corresponding sulphates:

$$H_2O + SO_3 \leftrightarrows H_2SO_4, \qquad CaO + SO_3 \rightarrow CaSO_4.$$

The union of an oxide of a non-metal with the oxide of a metal, in this fashion, is a general method of obtaining salts (compare p. 336).

Sulphur trioxide combines also with sulphuric acid to give **oleum,** or *fuming sulphuric acid,* $H_2S_2O_7$ (p. 429):

$$SO_3 + H_2SO_4 \rightarrow H_2S_2O_7.$$

The Contact Process for Sulphuric Acid. — The interaction of sulphur dioxide and oxygen is hastened by many substances, such as glass, porcelain, ferric oxide and, more especially, finely divided platinum, which remain themselves unchanged and simply act as contact or catalytic agents. The *contact process,* as this is called,

is now very extensively used in the manufacture of sulphuric acid.

The efficiency of the contact agent depends on the amount of surface it presents to the gases. The action may be illustrated by dipping asbestos in a solution of chloroplatinic acid and then heating the mineral in the Bunsen flame:

$$H_2PtCl_6 \rightarrow Pt + 2HCl \uparrow + 2Cl_2 \uparrow .$$

The platinum is thus spread in a fine gray powder on the fibers of the asbestos. The latter is placed in a tube (Fig. 17, p. 44), where a mixture of oxygen (or air) and sulphur dioxide may be passed over the heated material. The sulphur trioxide issues as vapor at the other end of the tube, where its presence is recognized by the dense fumes (droplets of sulphuric acid), produced when it meets the moisture in the air. The vapor can be condensed to liquid form in a cooled flask.

In practice the catalyst commonly employed is *platinum*, dispersed in a very finely-divided condition throughout a suitable supporting material, or *base*. The Grillo process uses as a base *magnesium sulphate*. This gives a catalytic mass just as active as platinized asbestos, and requires only one-hundredth the amount of platinum. With *silica gel* (p. 662) as a base, the platinum content of the contact mass can be still further reduced. *Vanadium pentoxide* V_2O_5 has recently come into extensive use as an alternative catalyst.

It is absolutely necessary, in employing the contact process, to remove from the sulphur dioxide all traces of substances such as arsenious oxide and similar impurities derived from the calcining of pyrite or some other mineral sulphide. The most minute quantities of these substances act as *poisons* on the catalytic agent, and soon render it quite inoperative. The sulphur dioxide is therefore very carefully purified before reaching the contact chamber. *Excess oxygen* is used in the air-SO_2 mixture, in order to drive the reaction more readily towards complete formation of SO_3 (compare p. 270). The temperature in the contact chamber is kept between 380° and 450°. The system has a tendency to get hotter during the reaction, owing to the heat evolved. This tendency, if unchecked, would lead to a decreased yield of sulphur trioxide; the cold entering gases are therefore first led over the outside of the pipes which contain the catalyst, in order to keep the temperature constant inside.

The issuing gases, consisting of SO_3 vapor mixed with excess

O_2 and inert N_2, are finally led into 97–99 per cent sulphuric acid, the concentration of the liquid being maintained at this point by a regulated influx of water. If oleum, or fuming sulphuric acid, is required, the addition of water is omitted.

It would seem to be simpler to dissolve the gaseous SO_3 in water, to give sulphuric acid $H_2O + SO_3 \rightarrow H_2SO_4$, rather than in 98 per cent sulphuric acid, but this cannot be done. The SO_3 in the mixture $N_2 + O_2 + SO_3$ is very incompletely absorbed by water. When a bubble of this mixture enters water, the latter evaporates into the bubble in the attempt to saturate the space occupied by the bubble with water vapor (p. 169). The water which so evaporates, however, combines immediately with the sulphur trioxide to form a fog, consisting of droplets of liquid sulphuric acid, and so more and more water evaporates into the bubbles. Now the molecules of SO_3, so long as they remain gaseous, move with great velocity, namely 292 meters per second at room temperature, and still faster in this hot gaseous mixture (see p. 122). Hence, all the molecules that escape combination with water vapor strike the wall of the bubble, and combine with liquid water, in a few seconds. The droplets of sulphuric acid forming the fog, however, are not molecules but large aggregates of molecules. They do not therefore move like the molecules of a gas, but are relatively stationary. The chance of their striking the wall of the bubble is thus reduced enormously. Hence, after the sulphur trioxide that escapes the water vapor has dissolved, the droplets of fog, carried by the excess of $N_2 + O_2$, can be bubbled through a whole series of vessels of water in succession without any significant amount of the droplets being removed. The fog can even be shaken in a flask with water, violently and continuously, without any appreciable solution. When the water is thrown, by the shaking, through the gas, the gas is split up into small bubbles, and driven about, but the fog particles move with the gas, so that the water seldom reaches them. On the other hand, when the mixture of gases bubbles through 97–99 per cent sulphuric acid, as is done in practice, there is practically no water available for evaporation, the sulphur trioxide remains gaseous, and its rapidly moving molecules in a few seconds have all plunged into the sulphuric acid and combined with it, either uniting with the 1 to 3 per cent of water present or, when oleum is made, uniting with the sulphuric acid to form $H_2S_2O_7$.

This case affords an admirable illustration of the importance of physics in practical chemistry. The chemical reactions occurs with water, but the physical condition of the fog of sulphuric acid prevents its dissolving and, if water were used in a factory, a large proportion of the sulphuric acid would pass with the excess of $N_2 + O_2$ into the air and be lost. In fact, it would kill vegetation, and make life unbearable in the neighborhood.

The **contact process,** as above described, is the best method for making a highly concentrated acid. For obtaining ordinary "oil of vitriol," however, the older **chamber process** is still used extensively.

History of Sulphuric Acid Manufacture.—Impure forms of sulphuric acid have been known for many centuries. In the fifteenth century it was made by distilling ferrous sulphate with sand. The product, however, contained

much water and sulphur dioxide. The first successful preparation of the substance commercially was made by Ward at Richmond-on-the-Thames (1758). The process consisted in burning a mixture of sulphur and saltpeter KNO_3 in a ladle suspended in a large glass globe partially filled with water. The gases which were evolved contained large quantities of sulphur dioxide and oxides of nitrogen, which, by interaction with atmospheric oxygen and water (see below), produced the sulphuric acid. The solution which was obtained, although it could be prepared of any desired concentration by the burning of a sufficient number of charges, was far from pure and was expensive, bringing thirteen shillings ($3.25) per pound. Subsequently a chamber lined with lead was substituted for the glass vessel. This reduced the price to about two shillings and sixpence ($0.60) per pound. The same principles are used in the modern "chamber process."

Chemistry of the Chamber Process. — The gases, the interactions of which result in the formation of sulphuric acid by this process, are: water vapor, sulphur dioxide, nitrous anhydride N_2O_3* (see p. 536), and oxygen. These are obtained, the first by injection of steam, the second usually by the burning of sulphur or the roasting of pyrite, the third from nitric acid HNO_3 (see below, p. 423), and the fourth by the introduction of air. The gases are thoroughly mixed in large leaden chambers, and the sulphuric acid forms droplets which fall to the floors. In spite of elaborate investigations, instigated by the extensive scale upon which the manufacture is carried on and the immense financial interests involved, some uncertainty still exists in regard to the precise nature of the chemical changes which take place. According to Lunge, supporting the view first suggested by Berzelius, the greater part of the product is formed by two successive actions, the first of which yields a complex compound that is decomposed by excess of water in the second:

$$H_2O + 2SO_2 + N_2O_3 + O_2 \rightarrow 2SO_2\begin{cases} O-H \\ O-NO \end{cases} \qquad (1)$$

The group — NO, nitrosyl, is found in many compounds. Here, if it were displaced by hydrogen, sulphuric acid would result. Hence this compound is called **nitrosylsulphuric acid:**

$$2SO_2\begin{cases} O-H \\ O-NO \end{cases} + H_2O \rightleftarrows 2SO_2\begin{cases} OH \\ OH \end{cases} + N_2O_3. \qquad (2)$$

* This gas is unstable, breaking up in part into nitric oxide NO and nitrogen tetroxide NO_2: $N_2O_3 \rightleftarrows NO + NO_2$. In this process, however, the mixture behaves as if it were all N_2O_3, and so only nitrous anhydride is named in this connection.

The equations (1) and (2) are not partial equations for one interaction, but represent distinct consecutive actions which can be carried out separately. In a properly operating plant, indeed, the nitrosylsulphuric acid is not observed. But when the supply of water is deficient, white "chamber crystals," consisting of this substance, collect on the walls.

The explanation of the success of this seemingly roundabout method of getting sulphuric acid is as follows: The direct union of sulphur dioxide and water to form sulphurous acid is rapid, but the action of free oxygen upon the latter, $2H_2SO_3 + O_2 \rightarrow 2H_2SO_4$, is relatively slow. Reaching sulphuric acid by the use of these two changes, although they constitute a direct route to the result, is not feasible in practice. On the other hand, both of the above actions, (1) and (2), happen to be much more speedy, and so, by their use, more rapid production of the desired substance is secured at the expense of a slight complexity.

The progress of the first action is marked by the disappearance of the brown nitrous anhydride and, on the introduction of water, the completion of the second stage results in the reproduction of the same substance. The nitrous anhydride takes part a large number of times in these changes, and so facilitates the conversion of a great amount of sulphur dioxide, oxygen, and water into sulphuric acid, without much diminution of its quantity. Some is unavoidably lost, however.

This loss of nitrous anhydride is made good by the introduction of nitric acid vapor into the chamber. The acid is made from concentrated sulphuric acid and commercial sodium nitrate $NaNO_3$:

$$NaNO_3 + H_2SO_4 \rightleftarrows HNO_3 \uparrow + NaHSO_4.$$

On account of the volatility of the nitric acid, a moderate heat is sufficient to remove it from admixture with the other substances, and its vapor is swept along with the other gases into the apparatus. The first reaction which this vapor undergoes may be written:

$$H_2O + 2SO_2 + 2HNO_3 \rightarrow 2H_2SO_4 + N_2O_3.$$

The N_2O_3 formed is now immediately available to take part in the successive cycles of reactions already discussed.

Relative Speed of Consecutive Reactions.—In consecutive reactions, as we have already mentioned (pp. 388–9), the second uses materials produced by the first, and it was noted that if the second action is as speedy as the first, or speedier, then no intermediate products will be detectable. This is the

case with the chamber process reactions, when sufficient steam is introduced, for under these circumstances no solid nitrosylsulphuric acid is deposited. If the second reaction is slower than the first, then the products of the first reaction will accumulate, and become noticeable.

The conception of consecutive reactions enables us to understand and remember many significant facts. For example, it was mentioned that when dry sulphur is oxidized, we obtain sulphur dioxide, but when moist sulphur is oxidized, by the air or otherwise, the only product is sulphuric acid (p. 402). This change may be formulated as proceeding in two stages:

$$S + O_2 + H_2O \rightarrow H_2SO_3,$$
$$2H_2SO_3 + O_2 \rightarrow 2H_2SO_4,$$

which are obviously consecutive reactions. Since oxidation of solid sulphur can proceed only on the surface, it is slow. Since the sulphurous acid is dissolved, and every molecule of it is accessible to the dissolved oxygen, or oxidizing agent, the second action should be speedier and consume the product of the first action as fast as it is formed. It is, therefore, quite natural that no sulphurous acid should be detectable when water is present.

Details of the Chamber Process. — The sulphur dioxide is produced in a row of furnaces *A* (Fig. 124). The gases from the various furnaces pass into one long dust-flue, in which they are mingled with the proper proportion of air, and deposit oxides of iron and of arsenic, and other materials which they transport mechanically. From this flue they enter the Glover tower *G*, in which they acquire the oxides of nitrogen. Having secured all the necessary components, excepting water, the gases next enter the first of the lead chambers *C*, large structures lined completely with sheet lead. These measure as much as 100 × 40 × 40 feet, and have a total capacity of 150,000 to 200,000 cubic feet. As the gases drift through these chambers they are thoroughly mixed, and an amount of steam considerably in excess of that actually required is generated in a boiler *D* and injected into the chambers at various points *E* and *F*. The sulphuric acid formed, along with the excess of steam, condenses and collects upon the floor of the chamber, whence it is run through a pipe P_1 into a reservoir R_1, while the unused gases, chiefly nitrous anhydride and nitrogen, the latter derived from the air originally admitted, find an exit into the Gay-Lussac tower *L*.

This is a tower about fifty feet in height, filled with tiles, over which *concentrated* sulphuric acid continually trickles. The object of this tower, to catch the nitrous anhydride and enable it to be reëmployed in the process, is accomplished by a reversal of action (2) on p. 422. The acid which accumulates in the vessel at the

bottom of this tower contains, therefore, nitrosylsulphuric acid, and by means of compressed air this acid is forced from a reservoir R_2 through a pipe P_2 up to a vessel at the top of the Glover tower G. A neighboring vessel at the top of this tower is filled with dilute sulphuric acid, forced up by compressed air from the reservoir R_1 through a pipe P_3 as required, and when the contents of both vessels are mixed by allowing their contents to trickle down through the tower, nitrous anhydride is once more set free by the interaction of the water in the dilute acid (action [2]). The Glover tower is filled with broken flint or tiles, in order that the descending liquid may offer a large surface to the hot gases ascending the tower, and thereby facilitate the acquisition by these gases of a

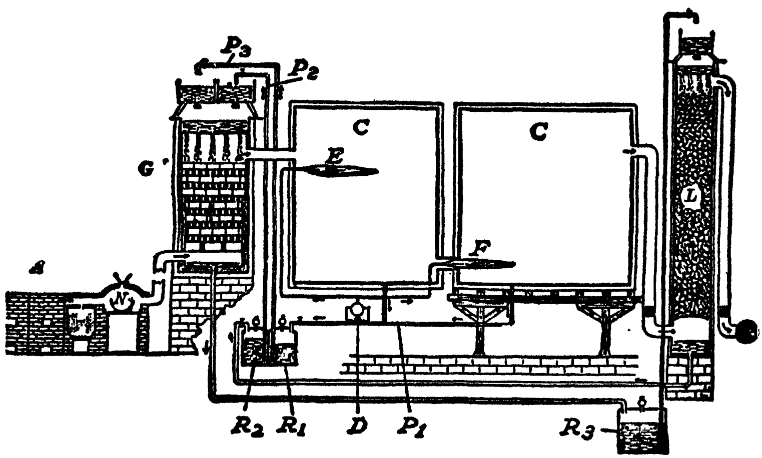


FIG. 124. Chamber Process for Manufacture of Sulphuric Acid.

sufficient quantity of nitrous anhydride. Their high temperature also causes a considerable concentration of the diluted sulphuric acid as it trickles downward. This concentrated acid, after traversing this tower, is run into a reservoir R_3, whence as much as is needed is forced by compressed air to the top of the Gay-Lussac tower L to be used once more for the absorption of nitrous anhydride.

To replace the part of the nitrous anhydride which is inevitably lost, fresh nitric acid is furnished by small open vessels N, containing sodium nitrate and sulphuric acid, placed in the flues of the pyrite-burners. About 4 kg. of the nitrate are consumed for every 100 kg. of sulphur.

Concentration of "Chamber Sulphuric Acid." — The acid which drains from the chambers into the reservoir R_1 ("chamber acid") contains but 60 to 70 per cent of sulphuric acid, and has a specific gravity of 1.5–1.62.

This crude sulphuric acid is applicable directly in some chemical manufactures, such as the preparation of superphosphates (p. 613). For many purposes, however, a more concentrated acid is required. (Some is available, of course, from the more concentrated product accumulating in the reservoir R_3.) Concentration of the chamber acid is effected by heating, to evaporate off water, in pans lined with lead, which are frequently placed over the pyrite-burners in order to economize fuel. The evaporation in lead is carried on until a specific gravity 1.7, corresponding to 77 per cent concentration, is reached. Up to this point the sulphate of lead formed by the action of the sulphuric acid produces a crust which protects the metal from further action. Beyond this point, however, the crust becomes appreciably soluble in the acid, and the lead is rapidly corroded. When a still more concentrated acid is wanted, other methods of driving off the water, such as the cascade system or the Gaillard tower, must therefore be employed.

The **cascade system** consists of a series of small silica or silicon-iron basins set over an inclined flue, and so placed that each basin delivers by a spout into the one below. The flue is heated by gas or coke firing at the lower end, and dilute acid is fed continuously into the basin at the top end. As the acid passes from basin to basin, it meets hotter and hotter conditions and becomes more and more concentrated.

The **Gaillard plant** consists essentially of a large hollow tower built of acid-resisting stone, and filled with small fragments of similar material. Dilute acid is sprayed in at the top, and meets hot furnace gases injected in at the bottom. Most of the water contained in the acid is carried off by these gases, and concentrated acid (**oil of vitriol,** with a specific gravity 1.83–1.84, and containing about 93.5 per cent H_2SO_4) collects at the bottom of the tower.

A more convenient method of obtaining very concentrated acid, which avoids the difficulties of evaporation entirely, is to add to the chamber acid the requisite quantity of **oleum,** prepared by the contact process already described

Physical Properties. — Pure hydrogen sulphate (100% sulphuric acid H_2SO_4) has a sp. gr. 1.85 at 15°. When cooled, it crystallizes (m.-p. 10.5°). At 150°–180° the acid begins to decompose, giving off fumes of sulphur trioxide. It "boils" at 270°, but loses more sulphur trioxide than water and finally yields an acid of constant boiling-point (338°) and constant composition (98.33 per cent). The vapor is largely decomposed into free water and sulphur trioxide, which recombine when it condenses.

Hydrogen sulphate mixes with water in all proportions, with considerable evolution of heat (see p. 210). Its solution (sulphuric acid) is thus much more stable (*i.e.*, it contains much less energy) than the pure substance, and hence the latter absorbs water greedily.

Commercial sulphuric acid is frequently brown in color on account of the presence of fragments of straw which have become charred and finally com-

pletely disintegrated. It contains also lead sulphate, which appears as a precipitate when the acid is diluted, as well as arsenic trioxide and oxides of nitrogen in combination, and many other foreign substances in small quantities. The pure sulphuric acid employed in chemical laboratories has received special treatment for the removal of these ingredients.

Chemical Properties of Hydrogen Sulphate. — 1. The compound is **not** exceedingly **stable**, for dissociation into water and sulphur trioxide, as noted above, begins far below the boiling-point. In the state of vapor it is practically completely dissociated at 416°, as is shown by the density of the vapor. When raised suddenly to a bright red heat it is broken up completely into water, sulphur dioxide, and oxygen (see p. 414).

2. Hydrogen sulphate combines vigorously with water to form several isolable hydrates, of which the most important is the **monohydrate,** H_2SO_4,H_2O (m.-p. 10°). On this account, very concentrated sulphuric acid is able to take the elements of water from compounds containing hydrogen and oxygen, especially those containing these elements in the proportion 2H : 1O (see p. 603). Thus paper, which is largely cellulose $(C_6H_{10}O_5)_y$, wood (which contains much cellulose) and sugar $C_{12}H_{22}O_{11}$ are charred by it, and carbon is set free:

$$C_{12}H_{22}O_{11} \rightarrow 12C + 11H_2O.$$

For the same reason, concentrated sulphuric acid is used in drying gases with which it does not interact. It is the most common **dehydrating agent** used in chemistry.

3. On account of the large quantity of oxygen which hydrogen sulphate contains, and its instability when heated, it also behaves as an **oxidizing agent.** This property has already been illustrated in connection with the action of the concentrated acid upon carbon, sulphur, and copper (p. 415), zinc (p. 133), hydrogen sulphide (p. 404), hydrogen iodide (p. 352), and hydrogen bromide (p. 347). The hydrogen sulphate is in consequence reduced to sulphur dioxide, and even to free sulphur or hydrogen sulphide. The metals, from the most active down to silver (p. 142), are capable of reducing it at moderately high temperatures, the sulphates * being formed. The more active metals, like zinc, reduce it to hydrogen sulphide, the less active, like copper, give sulphur dioxide. Gold and platinum

* Note that the sulphates, and *not* the oxides of the metals, are produced. Oxides of metals could not be *formed in* concentrated sulphuric acid, because they interact with the latter much more vigorously than do the metals, to give the sulphates (compare p. 257).

alone do not interact with it. Free hydrogen itself is oxidized to water when passed into hydrogen sulphate at 160° : $H_2SO_4 + H_2 \rightarrow SO_2 + 2H_2O$.

Chemical Properties of Aqueous Hydrogen Sulphate. — 1. Except in concentrated solutions (normal or above) oxidizing effects are not encountered. Ionization takes place in two stages:

$$H_2SO_4 \rightleftarrows H^+ + HSO_4^- \rightleftarrows 2H^+ + SO_4^=.$$

2. In dilute aqueous solution, sulphuric acid is much more active as *an acid* than is sulphurous acid, but is somewhat inferior in this respect to hydrochloric acid HCl and nitric acid HNO_3. Like other active, soluble acids, its solution turns litmus red, gives hydrogen upon addition of active metals, and enters into double decomposition with bases and salts. Thus, insoluble barium sulphate is obtained as a white precipitate by the action of dilute sulphuric acid on any soluble barium salt:

$$BaCl_2 + H_2SO_4 \rightarrow BaSO_4 \downarrow + 2HCl.$$

Any soluble sulphate will, of course, give the same precipitate with barium chloride, and the action is used as a **test** for this ion. Some other salts of barium are also insoluble in water, but the sulphate is recognized by the fact that it is too insoluble to be acted upon by dilute pure hydrochloric acid or nitric acid. The other insoluble salts of barium interact with these aids and dissolve. The addition of one of these acids is therefore part of the **test** for $SO_4^=$ ion.

3. On account of its high boiling-point, the double decompositions of the concentrated acid can be *used for preparing more volatile acids:*

$$NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl \uparrow \text{ (gas at room temp.)}.$$
$$NaNO_3 + H_2SO_4 \rightarrow NaHSO_4 + HNO_3 \uparrow \text{ (volatile at 86°)}.$$

4. Since hydrogen sulphate is **dibasic** (p. 405), it forms both acid and normal salts, such as $NaHSO_4$ and Na_2SO_4. The acid sulphates are called also bisulphates, because they contain twice as large a proportion of SO_4 to Na, and require twice as much sulphuric acid for their preparation as do the neutral sulphates.

Sulphates. — The **acid sulphates** may be produced either by adding to dilute sulphuric acid half an equivalent of a base, and evapo-

rating: $NaOH + H_2SO_4 \rightarrow H_2O + NaHSO_4$, or by actions in which another acid is displaced, as in making hydrogen chloride (p. 225). These salts are acid in reaction, as well as in name.

When acid sulphates, such as $NaHSO_4$, are heated, water is given off and a *pyrosulphate* (Greek prefix, *fire*) remains:

$$2NaHSO_4 \rightarrow Na_2S_2O_7 + H_2O.$$

The pyrosulphates are salts of oleum, or fuming sulphuric acid, which has already been mentioned. Oleum possesses all the dehydrating and oxidizing powers of sulphuric acid in an accentuated form, and is widely used in the industries on account of these properties. Oleum (fuming sulphuric acid) was also employed to conceal ships against submarines during the Great War. A finely-divided spray of oleum was injected into the smoke-stacks of the vessel and carried by the hot gases issuing therefrom into the atmosphere in the form of vapor. In contact with the cool moist air over the ocean, this vapor condensed to give tiny droplets of sulphuric acid, which hung over the surface as a very persistent mist, extremely difficult to distinguish from a natural fog.

The **normal** (or neutral) **sulphates** are obtained by complete neutralization and evaporation, or by the total displacement of another acid when a sufficient amount of the salt and a higher temperature are used:

$$NaCl + NaHSO_4 \rightleftarrows Na_2SO_4 + HCl\uparrow.$$

They may also be made by precipitation, by oxidation of a sulphide at a high temperature, $PbS + 2O_2 \rightarrow PbSO_4$, or by addition of sulphur trioxide to the oxide of a metal.

Normal sulphates of the heavy metals decompose when heated, giving off either sulphur trioxide, or sulphur dioxide and oxygen according to the temperature of the decomposition (see p. 419). The sulphates of the more active metals and of lead, however, are not affected by heating.

When a sulphate, or indeed any salt of a sulphur acid, is heated strongly with carbon, the oxygen is removed and a sulphide remains: $Na_2SO_4 + 4C \rightarrow Na_2S + 4CO$. Upon this is founded a general **test** for the presence of sulphur in any substance. The material to be tested is mixed with sodium carbonate. A small amount of the mixture is placed on the end of a match, which has been charred and rendered partially incombustible by previous applica-

tion of sodium carbonate. When the end of the match is now held in the reducing part of the Bunsen flame, the compound of sulphur, if it contains oxygen, is reduced to the form of sulphide. This, by interaction with the carbonate, gives sodium sulphide, Na_2S. When the product of the reduction is placed upon a silver coin and moistened, the sodium sulphide, if present, produces a black stain of silver sulphide. This is known as the **hepar test,** hepar being an old name for a sulphide.

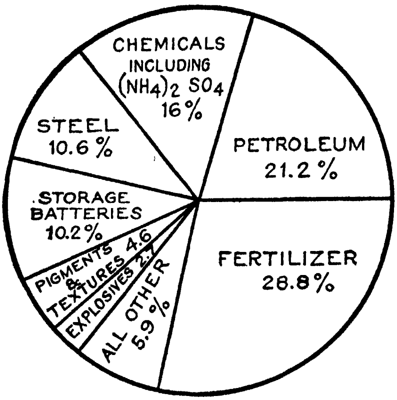


FIG. 125. Distribution of Sulphuric Acid in Industry.

Uses of Sulphuric Acid. — The acid has innumerable applications, some of which will be taken up in detail in later chapters.

It is employed in almost every chemical industry (see Fig. 125), approximately 6,000,000 tons being produced yearly in the United States alone. It is used in the manufacture of sulphates, hydrochloric acid, nitric acid, sodium carbonate, etc., also in refining petroleum, in making fertilizers and dyes, in bleaching, electroplating and so on. Its dehydrating power is especially valuable in making explosives (pp. 652–4).

OTHER ACIDS OF SULPHUR

Next in importance to sulphurous and sulphuric acids come hyposulphurous acid, thiosulphuric acid and persulphuric acid. The compositions of the acids show their relationships:

Hyposulphur*ous* acid,	$H_2S_2O_4$.	Sodium hyposulph*ite*,	$Na_2S_2O_4$.
Sulphur*ous* acid,	H_2SO_3.	Sodium sulph*ite*,	Na_2SO_3.
Sulphur*ic* acid,	H_2SO_4.	Sodium sulph*ate*,	Na_2SO_4.
Thiosulphur*ic* acid,	$H_2S_2O_3$.	Sodium thiosulph*ate*,	$Na_2S_2O_3$.
Persulphur*ic* acid,	$H_2S_2O_8$.	Sodium persulph*ate*,	$Na_2S_2O_8$.

Thiosulphuric acid (Greek *θεῖον*, sulphur) is so named because it contains one unit of sulphur in place of one of the units of oxygen of sulphuric acid. Besides the above we have also a series of poly-

thionic acids, namely: dithionic acid $H_2S_2O_6$, trithionic acid $H_2S_3O_6$, tetrathionic acid $H_2S_4O_6$, and pentathionic acid $H_2S_5O_6$.

Hyposulphurous Acid $H_2S_2O_4$. — The zinc salt of this acid crystallizes out when zinc dust acts upon a solution of sulphur dioxide in absolute alcohol:

$$Zn + 2SO_2 \rightarrow ZnS_2O_4.$$

Moissan found that when sulphur dioxide was led over sodium hydride (p. 450), sodium hyposulphite was formed: $2NaH + 2SO_2 \rightarrow Na_2S_2O_4 + H_2$.

Commercially, a solution containing the sodium salt is made by the interaction of zinc with a solution of sodium bisulphite charged with excess of sulphur dioxide:

$$2NaHSO_3 + SO_2 + Zn \rightarrow Na_2S_2O_4 + ZnSO_3 + H_2O.$$

The salts are rapidly oxidized by the air, giving sulphites and then sulphates. The above solution of sodium hyposulphite is used in indigo dyeing, and with other vat dyes, on account of its high reducing power. Indigo $C_{16}H_{10}N_2O_2$, which is insoluble, is reduced by the salt to indigo-white $C_{16}N_{12}N_2O_2$ which passes into solution:

$$Na_2S_2O_4 + 2H_2O + C_{16}H_{10}N_2O_2 \rightarrow 2NaHSO_3 + C_{16}H_{12}N_2O_2.$$

When cloth saturated with the mixture, however, is exposed to the air, the indigo-white undergoes oxidation, and blue, insoluble indigc is formed once more (see Dyeing).

The acid is formed when sulphurous acid surrounds the negative electrode in an electrolytic cell:

$$2SO_3^- + 4H^+ \rightarrow S_2O_4^= + 2H_2O,$$

and was first named (after the discoverer) Schützenberger's acid. The sodium salt is formed in the same way from sodium bisulphite.

Thiosulphuric Acid $H_2S_2O_3$. — This acid is not known in the free condition, but its salts are in common use in the laboratory and commercially. Sodium thiosulphate, for example, is prepared by boiling a solution of sodium sulphite with free sulphur. The action resembles the addition of oxygen to sulphurous acid:

$$Na_2SO_3 + S \rightarrow Na_2S_2O_3 \quad \text{or} \quad SO_3^= + S \rightarrow S_2O_3^=.$$

Sodium thiosulphate (in the form of the hydrate $Na_2S_2O_3{,}5H_2O$, popularly, but incorrectly, named "hypo") is used in "fixing" photographs (p. 810). It has also been employed on a large scale at Hollywood in artificial skating rinks, which allow winter scenes to be reproduced at summer temperatures.

By the addition of acids to a solution of sodium thiosulphate, the thiosulphuric acid is set free, but the latter instantly decomposes, giving a precipitate of sulphur:

$$Na_2S_2O_3 + 2HCl \rightleftarrows H_2S_2O_3 + 2NaCl,$$
$$H_2S_2O_3 \leftrightarrows S\downarrow + H_2SO_3.$$

Even carbon dioxide from the air, giving carbonic acid (p. 374), produces this effect slowly in fixing solutions. The actions being reversible, preliminary addition of a sulphite to the solution helps to sustain the reverse action, in which sulphurous acid is a factor, and so preserves the solution. The delay in the appearance of the precipitate of sulphur in dilute solutions is due to the temporary existence of a colloidal solution (compare p. 208) of the free element. This is shown by the fact that instant neutralization of the free acid does not prevent the ultimate appearance of the sulphur.

Iodine acts upon sodium thiosulphate solution, giving sodium tetrathionate:

$$2Na_2S_2O_3 + I_2 \rightarrow 2NaI + Na_2S_4O_6.$$

This action is used, by employment of a standard solution of sodium thiosulphate, for estimating quantities of free iodine in analysis. The disappearance of the color of the latter indicates that a sufficient amount of the salt has been employed. When chlorine-water (p. 245) is used, the oxidation is more complete. The products are sodium sulphate, sulphuric acid, and hydrochloric acid:

$$Na_2S_2O_3 + 4HOCl + H_2O \rightarrow Na_2SO_4 + H_2SO_4 + 4HCl.$$

In consequence of the very great amount of free chlorine which the sodium thiosulphate is thus able to transform, it is employed, as *antichlor,* for the purpose of removing chlorine from bleached fabrics.

Persulphuric Acid $H_2S_2O_8$. — This, like the other acids just mentioned, is unstable and can be kept only in dilute solution. Its salts, however, are coming into use for commercial purposes and

for "reducing" negatives in photography. The salts are prepared by electrolyzing sodium-hydrogen sulphate $NaHSO_4$ in concentrated solution, using a very high current density (Hugh Marshall). The persulphuric acid, formed by the union of the negative ions in pairs as they are discharged on the anode,

$$2HSO_4^- \rightarrow H_2S_2O_8 + 2\Theta,$$

undergoes double decomposition with the excess of sodium bisulphate, and the less soluble sodium persulphate crystallizes out. The other salts are made by double decomposition from this one.

The persulphates decompose readily when heated, yielding pyrosulphates and oxygen:

$$2K_2S_2O_8 \rightarrow 2K_2S_2O_7 + O_2.$$

Persulphuric acid is now extensively used in the manufacture of hydrogen peroxide. In one process a 40 per cent solution, obtained by the high current-density electrolysis of sulphuric acid, is distilled under reduced pressure and hydrolyzes as follows:

$$H_2S_2O_8 + 2H_2O \rightarrow 2H_2SO_4 + H_2O_2.$$

In another process an acid solution of ammonium sulphate is electrolyzed, potassium sulphate is added, and the potassium persulphate precipitated is distilled with sulphuric acid under reduced pressure. By this method concentrated solutions of H_2O_2 are obtained directly.

Polythionic Acids. — Di-, tri-, tetra-, and pentathionic acids (p. 431), are all formed simultaneously (along with free sulphur) when sulphur dioxide and hydrogen sulphide gases are passed alternately into water, although the gases themselves (p. 404) interact to produce simply free sulphur and water:

$$H_2S + 3SO_2 \rightarrow H_2S_4O_6,$$
$$2H_2S + 6SO_2 \rightarrow H_2S_3O_6 + H_2S_5O_6,$$
$$3H_2S + 9SO_2 \rightarrow H_2S_2O_6 + 2H_2S_5O_6.$$

Most of these acids and their salts are of minor interest and need not be discussed.

The production of sodium tetrathionate by the action of iodine upon sodium thiosulphate has already been mentioned (p. 432).

When manganese dioxide is treated with cold sulphurous acid, it interacts rapidly and a solution of manganous dithionate is obtained:

$$MnO_2 + 2H_2SO_3 \rightarrow MnS_2O_6 + 2H_2O.$$

The salts of these acids are in many cases fairly stable, but the acids themselves decompose readily when set free.

Compounds of Sulphur and Chlorine. — When chlorine gas is passed over heated sulphur, it is absorbed and **sulphur monochloride,** a reddish-yellow liquid, boiling at 138°, is obtained. The molecular weight of this substance, as shown by the density of its vapor, indicates that it possesses the formula S_2Cl_2. When thrown into water, it is rapidly hydrolyzed, producing sulphur dioxide and sulphur: $2S_2Cl_2 + 2H_2O \rightarrow SO_2 + 4HCl + 3S$.

Sulphur itself dissolves very freely in the monochloride, and the solution is employed in vulcanizing rubber.

By surrounding sulphur monochloride with a freezing mixture, and treating it with excess of chlorine, a liquid **dichloride** SCl_2 and a **tetrachloride** SCl_4 can be formed. Both are unstable.

By the action of sulphur dioxide gas upon phosphorus pentachloride, part of the oxygen in the former is replaced by chlorine:

$$SO_2 + PCl_5 \rightarrow SOCl_2 + POCl_3.$$

The products are **thionyl chloride** and phosphorus oxychloride. The former is a colorless liquid, boiling at 78°, and is separated from the latter (b.-p. 107°) by fractional distillation (see Petroleum). It is decomposed immediately on contact with water:

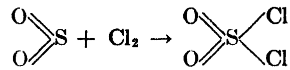
$$SOCl_2 + 2H_2O \rightarrow H_2SO_3 + 2HCl.$$

Sulphur dioxide and chlorine gases unite when exposed to direct sunlight to form a liquid known as **sulphuryl chloride** SO_2Cl_2. When camphor is introduced into the vessel the union takes place much more rapidly, owing to some catalytic effect of this substance. The compound is a colorless liquid, boiling at 69°. With water it gives sulphuric acid and hydrogen chloride by hydrolysis (p. 231). When a strictly limited amount of water is supplied a partial action of the same nature occurs, and the product is known as **chlorosulphuric acid:**

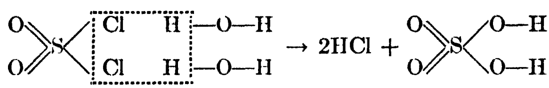
$$SO_2Cl_2 + H_2O \rightarrow SO_2{<}^{Cl}_{OH} + HCl.$$

This intermediate compound (which resembles *oleum* in its physical properties) may be formed also by the addition of hydrogen chloride to sulphur trioxide.

Graphic Formula of Sulphuric Acid. — The actions just mentioned give a clue to the constitution of sulphuric acid. Since chlorine does not combine directly with oxygen, but does combine readily with sulphur, we may assume that, in the formation of sulphuryl chloride, $SO_2 + Cl_2 \rightarrow SO_2Cl_2$, the chlorine unites more intimately with the sulphur in the molecule SO_2:



The action of water upon the product is presumably similar to that of water on phosphorus trichloride (p. 231):



The last is called the **structural formula** of sulphuric acid. It is not thereby implied that the atoms in its molecules are attached precisely in this manner (see p. 146), but rather that the *chemical behavior* of the substance, as being partly an oxide and partly a hydroxide of sulphur, is symbolized in this fashion. Such **graphic formulæ** are of great value in expressing the chemical behavior of the complex compounds of carbon (p. 578).

Exercises. — 1. What ground is there for assigning the formula SO_2 instead of S_2O_4 to sulphur dioxide (p. 415)?

2. Explain why nitric acid is completely displaced by the action of sulphuric acid on sodium nitrate (p. 423).

3. What are the relative volumes, (*a*) of sulphur dioxide and nitrogen (p. 13) resulting from the roasting of pyrite (p. 414), (*b*) of air and sulphur dioxide in making sulphuric acid, (*c*) of nitrogen (left) to sulphur dioxide (used) in making sulphuric acid, when pyrite is the source?

4. Give two reasons why boiling sulphuric acid, when spilt upon the flesh, causes most serious burns.

5. Why is it not desirable to make chamber sulphuric acid of a concentration higher than 60–70 per cent?

6. Justify the nomenclature in the case of hyposulphurous and persulphuric acids.

7. Given normal solutions of sodium hydroxide and sulphuric acid, how would you proceed to form: (*a*) sodium sulphate, (*b*) sodium bisulphate?

8. Explain, by means of ionic equations, why a solution of sodium bisulphite shows an acid reaction, and why a solution of sodium sulphite shows an alkaline reaction.

9. Employ each of the two methods described on pp. 378–9 to balance the following skeleton equations:

(*a*) $H_2SO_4 + Cu \rightarrow H_2O + SO_2 + CuSO_4$.
(*b*) $H_2SO_4 + Zn \rightarrow H_2O + H_2S + ZnSO_4$.

10. What volume of sulphur dioxide at 20° and 760 mm. will be obtained by adding excess of concentrated H_2SO_4 to 10 g. of sodium-hydrogen sulphite? What volume of water will be required to dissolve this gas under the same conditions (p. 415)?

11. Tabulate the gases you have so far investigated into two classes: (*a*) those which are completely removed from their aqueous solution by boiling, (*b*) those which give constant-boiling mixtures. Examine your lists with reference to the table on p. 317. What conclusions may be drawn (pp. 339–40)?

12. What weight of 98 per cent sulphuric acid can be obtained by burning 1000 kg. of pyrite FeS_2 and putting the resultant sulphur dioxide through the contact process? Assume that the pyrite is 90 per cent pure, and that the efficiency of the process is 99 per cent.

13. Use the ion and electron method to write balanced equations for the reduction, by means of sulphurous acid, of (*a*) hydrogen peroxide, (*b*) potassium permanganate, (*c*) potassium dichromate.

14. Sulphurous acid is a good reducing agent. Sulphuric acid is a good oxidizing agent. Explain why nothing happens when the two substances are mixed.

15. Why is it safer, when you want to mix concentrated sulphuric acid and water, to add the acid to the water, rather than the water to the acid?

16. Apply the ion and electron method of analyzing and balancing complex equations to the oxidation, by means of sulphuric acid, of (*a*) sulphur, (*b*) carbon, (*c*) hydrogen iodide.

17. Correlate the main uses of sulphuric acid with its physical and chemical properties.

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CHAPTER XXV

SELENIUM AND TELLURIUM. THE PERIODIC SYSTEM

In an earlier chapter (p. 343) we saw that the elements fluorine, chlorine, bromine and iodine exhibited striking similarities in their chemical behavior, and we grouped these four elements together under the name of the halogen family. Now there are two rather rare elements, **selenium** (Se, at. wt. 79.0) and **tellurium** (Te, at. wt. 127.6), which resemble sulphur very markedly in their chemical relations.

Occurrence and Properties of Selenium Se. — Selenium (Greek, *the moon*) occurs free in some specimens of native sulphur, and in combination often takes the place of a small part of the sulphur in pyrite (FeS_2). It is found free in the dust flues of the pyrite-burners of sulphuric acid works. The main source of selenium (and of tellurium), however, is the anode mud which is obtained as a by-product in the electrolytic refining of copper (p. 794).

Selenium exists in several allotropic modifications, the most familiar forms being the red precipitated variety, which is amorphous and soluble in carbon disulphide, and the lead-gray, semimetallic variety, obtained by slow cooling of melted selenium, which is insoluble, and melts at 217°. In the latter form it has some capacity for conducting electricity, which is greatly increased by exposure to light in proportion to the intensity of the illumination. A photometer, using this property, has been devised by Joel Stebbins (1914), for measuring the relative intensity of the light of different stars. Selenium boils at 690°, and at high temperatures has a vapor density corresponding to the formula Se_2.

The element combines directly with many metals, burns in oxygen to form selenium dioxide, and unites vigorously with chlorine.

Small quantities of selenium are employed in glass works to neutralize the green tint imparted by traces of iron (p. 665). Addition of larger amounts gives ruby-red glass, used for ornamental purposes. Selenized rubber is very resistent to abrasion and is also useful as a fire-proof covering for cables.

Compounds of Selenium. — Ferrous selenide, made by heating iron filings with selenium (compare p. 22), when treated with concentrated hydrochloric acid, gives hydrogen selenide:

$$FeSe + 2HCl \leftrightarrows H_2Se \uparrow + FeCl_2.$$

The compound is a poisonous gas, which possesses an odor recalling rotten horse-radish, and is soluble in water. The solution is faintly acid in reaction, and deposits selenium when exposed to the action of the air (compare p. 405). Other selenides, which, with the exception of those of potassium and sodium, are insoluble in water, may be precipitated by leading the gas into solutions of soluble salts of appropriate metals (compare p. 411).

The **dioxide** SeO_2 is a solid substance, formed by burning Se. Selenious acid H_2SeO_3 may be made by dissolving the dioxide in hot water, or by oxidizing selenium with boiling nitric acid. Unlike sulphur (p. 402), the element gives little of the higher acid H_2SeO_4 by this treatment. The acid is reduced by sulphurous acid to selenium: $H_2SeO_3 + 2H_2SO_3 \rightarrow 2H_2SO_4 + H_2O + Se$.

The **trioxide** SeO_3 is extremely hygroscopic, and has only recently been isolated. **Selenic acid** H_2SeO_4, a white solid, is made in solution by oxidizing silver selenite with bromine-water:

$$Br_2 + H_2O + Ag_2SeO_3 \rightarrow 2AgBr \downarrow + H_2SeO_4.$$

It is much more powerful than sulphuric acid as an oxidizing agent, and, even in dilute solution, liberates chlorine from hydrochloric acid: $H_2SeO_4 + 2HCl \rightarrow H_2SeO_3 + H_2O + Cl_2$. Sulphuric acid (compare p. 428), on the other hand, is an oxidizing agent only in somewhat concentrated form, and even then it can oxidize hydrobromic acid (p. 347), but not hydrochloric acid.

The **chlorides** of selenium are formed by direct union of the elements. The tetrachloride, a yellow crystalline substance, is formed when the monochloride is heated: $2Se_2Cl_2 \rightarrow 3Se + SeCl_4$, the behavior in the case of sulphur chlorides being just the inverse of this (p. 434).

Selenium oxychloride $SeOCl_2$ is a very interesting compound, readily formed by the partial hydrolysis of the **tetrachloride** $SeCl_4$:

$$SeCl_4 + H_2O \rightarrow SeOCl_2 + 2HCl.$$

It is a highly corrosive and remarkably active liquid (Lenher).

Tellurium Te.—Tellurium (Latin, *the earth*) occurs in **sylvanite** in combination with gold and silver. It is a white, metallic, crystalline substance, melting at 452° (b.-p. 1400°). The free element unites with metals directly, and burns in air to form the dioxide. Small amounts of tellurium are added to the lead which is used in water pipes, since its presence increases the resistance of the lead to corrosion and also increases its tensile strength, thus lessening the risk of bursting in cold weather.

The compounds of tellurium are similar in composition and mode of preparation to those of selenium. Some differences in chemical behavior are significant, however. Thus, **tellurious acid** H_2TeO_3 is a very feeble acid and is also somewhat basic, a sulphate ($2TeO_2$, SO_3) and a nitrate ($Te_2O_3(OH)NO_3$) being known. In this respect it differs markedly from sulphurous acid. **Telluric acid** does not affect indicators, and is therefore actually more feebly acidic than is hydrogen sulphide. **Tellurium trioxide** TeO_3 is a yellow solid, which shows no tendency to recombine with water, in this respect resembling silica (p. 660). Tellurates of the alkali metals may be made by heating the tellurites with potassium or sodium nitrate: $K_2TeO_3 + KNO_3 \rightarrow K_2TeO_4 + KNO_2$.

Tellurium tetrachloride $TeCl_4$, although hydrolyzed by water, exists in solution with excess of hydrogen chloride: $TeCl_4 + 3H_2O \rightleftarrows H_2TeO_3 + 4HCl$, showing the tellurious acid to be basic in properties and the element tellurium to be, to a certain degree, a metallic element (see p. 681).

The Chemical Relations of the Sulphur Family.—It will be evident from the above paragraphs that both selenium and tellurium, as stated at the beginning of the chapter, resemble sulphur very markedly in their chemical properties. Both give compounds with hydrogen, hydrogen selenide H_2Se and hydrogen telluride H_2Te, corresponding with hydrogen sulphide H_2S, but less stable. Both give compounds with oxygen, selenium dioxide SeO_2 and tellurium dioxide TeO_2, corresponding with sulphur dioxide SO_2. These dioxides dissolve in water to form weak acids similar to sulphurous acid. These acids, again, can be oxidized to yield selenic acid H_2SeO_4 and telluric acid H_2TeO_4, analogous to sulphuric acid H_2SO_4. All these compounds show gradations in properties, as we go upwards in atomic weights from S to Te, which are very reminiscent of the gradations encountered in a series of halogen compounds, such as HCl, HBr, HI.

Furthermore, just as we have in the halogen family a first member with rather irregular habits, *fluorine*, so we note in the sulphur family a corresponding light element showing decided peculiarities, *oxygen*. Oxygen forms a compound with hydrogen H_2O, which is akin to H_2S in being a weak acid and, as might be predicted, is much more stable. The metallic oxides are very similar in their properties to the metallic sulphides. Ozone may be regarded as oxygen dioxide OO_2, analogous to sulphur dioxide SO_2. The family resemblance in other compounds, however, is more difficult to trace.

The question naturally arises: Can we group *all* of the elements into families like the halogen family and the sulphur family? If so, then we shall lighten considerably the burden of chemical facts that we need to remember, for the behavior of one element in a family will suggest to us immediately how the other members of the same group will act under similar conditions. Classification of this kind is part of the method of science, and furnishes a very useful guide in investigation.

Metallic and Non-metallic Elements. — Thus far we have found the division into metallic and non-metallic elements very serviceable for classification in terms of chemical relations (p. 393). This distinction we shall continue to employ. **The metallic, or positive elements** (p. 174), form positive radicals and ions containing no other element (see p. 290). Thus the metals give sulphates, nitrates, carbonates, and other salts, which furnish a metallic ion, such as Na^+ or K^+, together with the ions $SO_4^=$, NO_3^-, and $CO_3^=$. Their hydroxides, KOH, $Ca(OH)_2$, etc., give the same metallic ion, and the rest of the molecule forms hydroxyl-ion. That is to say, their hydroxides are bases and their oxides are basic. The metallic elements often enter, but only *with other elements*, into the composition of a negative ion, as is the case with manganese in $K.MnO_4$, with chromium in $K_2.Cr_2O_7$, and with silver in $K.Ag(CN)_2$.* But the most definitely metallic elements form with oxygen such a negative ion only while exhibiting a *different valence* from that which they possess when acting as positive elements. Thus, manganese when a positive element has the valences two and three, MnO and Mn_2O_3, $Mn.Cl_2$ and $Mn.Cl_3$, $Mn.SO_4$ and $Mn_2.(SO_4)_3$, etc., while in permanganates we have potentially the oxide Mn_2O_7, (K_2O,

* The mode of division into ions is shown by the position of the period in the formula.

CHAPTER XXVI

THE ATMOSPHERE AND ITS INERT COMPONENTS. RADIOACTIVITY

The components of the air may be conveniently divided into *regular* components and *accidental* components. The regular components, again, consist of three which are present in practically the same proportions in all samples, and three (namely water, carbon dioxide and dust) which vary markedly in quantity.

Components Present in Constant Proportions. — The components whose proportions are practically invariable are nitrogen, oxygen, and the group of inert gases. When the variable components are removed, the proportions of the constant ones are as follows:

	By Volume	By Weight
Nitrogen...............	78.06	75.5
Oxygen.................	21.00	23.2
Argon, etc.............	0.94	1.3

The determination of the **oxygen** by allowing iron to rust in air (p. 13), and measuring the residual gas, is not capable of application in an exact manner. A stick of phosphorus, enclosed in wire gauze (p. 505), removes the oxygen rather slowly. It is better to use a large amount of phosphorus in the form of thin wire. In this way a great surface is obtained, and the absorption of oxygen from a sample of air may be carried out in a few seconds. The passage of purified air over heated copper has also been used for the same purpose. When this method is employed, the volume of the nitrogen and argon which survives the action of the copper is measured, while the increase in weight of the copper, through formation of cupric oxide, gives the weight of the oxygen which was originally mixed with it.

Still another method, which is in constant employment in the analysis of mixtures of gases, may also be applied to the air. It consists in bringing a measured volume of air in contact with an alkaline solution of potassium pyrogallate (p. 810), which quickly absorbs the oxygen, and noting the decrease in volume.

In the air taken from mines, from mountain tops, from the surface of the sea, and from inland regions, the proportion of oxygen to the residual gas is

found to be fairly constant, although easily perceptible differences are noted. The percentage of oxygen in dried air ranges between 20.26 and 21.00, the latter being the proportion in normal air.

When the residual gas is led slowly through a heated tube containing magnesium, the **nitrogen** unites with the metal to form the solid nitride Mg_3N_2, and only about 10 c.c. out of every liter remains uncombined. This residuum is **argon,** mixed with small traces of other gases belonging to the helium family (see p. 462).

Air a Mixture. — Since the main components of air were not definitely identified until the end of the eighteenth century, we can understand why the substance was for long considered to be an element. The experiments which we have described (pp. 13, 88, 453) in which the oxygen was removed from the air and the nitrogen remained, do not prove *conclusively* that the original constituents were present simply in mechanical mixture. They might have been combined, and the combustion of phosphorus, for example, might have represented the removal of oxygen from combination with nitrogen and its appropriation by the phosphorus. It may be well, therefore, to point out some more cogent reasons which lead us to regard the air as a mixture:

1. When two substances enter into chemical combination, the new body invariably has different physical properties from either of the original ones. Each of the substances in air, however, has precisely the same properties which it exhibits when free, separate, and pure. This is characteristic of a mixture. Thus, there is no simple relation between the *refractive power* for light which a compound possesses and the refractive powers of its constituents. In the case of air, however, the refractive power is exactly that which we should calculate from the refractive powers of the components, taking into account the proportions of them which air contains.

Again, the nitrogen and oxygen *dissolve* independently in water in proportion to their solubilities and partial pressures (p. 220). If the air were a compound, it would dissolve as a whole, and the relative proportions of the components would not be changed by the process. Also, the *density* of air is precisely that which we find by calculation from the known proportions and several densities of the components. Likewise, when liquefied air is allowed to evaporate in a suitable apparatus, the nitrogen, being more volatile, can be separated from the oxygen. When the oxygen, in turn, is allowed to evaporate, the carbon dioxide and water remain as solids, frozen at this low temperature. No compound of nitrogen and oxygen is found.

2. The proportion by volume in which the gases are found in the air is not so simple as the proportions which we observe in cases of chemical combination. The proportion is close to 4 : 1, but not exactly 4 : 1. Besides, as we have seen, the proportion is not perfectly constant.

3. The composition of air by weight is such that it *cannot be represented by a chemical formula.* This shows that the law that, in chemical compounds, the proportions can be represented by multiples of the atomic weights by whole numbers (p. 187), does not apply to air, and air is consequently not a chemical compound.

In spite of the fact that air is a mixture, the composition of the air is remarkably uniform (see p. 453). The uniformity is due to constant mixing by the winds. The steadiness of the composition from year to year is due to the fact that, although decay and combustion continually remove oxygen and add carbon dioxide, vegetation as continually consumes the latter and restores the former (p. 598). The mass of carbon dioxide in the whole atmosphere of the planet, about 2450 thousand million tons, is so great that the amounts added and removed by the agencies just mentioned are small by comparison.

To expand an illustration made by Graham, if we imagined the air to be divided by magic into layers, all at one atmosphere pressure, and with the heavier components below, we should have: On the earth, five inches of water; above that, thirteen feet of carbon dioxide; above that, ninety yards of argon; above that, one mile of oxygen; and on the top four miles of nitrogen.

The Water Vapor. — The proportion of water vapor in the air is exceedingly *variable.* When air becomes cool, the moisture *separates* in **cloud** and **fog,** which are composed of minute drops of liquid water. When much moisture is condensed, the drops are larger and fall as **rain.** When they fall through a cold region, they freeze to **hail.** When condensation takes place in air already below 0°, the fog is composed of solid and not of liquid particles. The hexagonal crystalline structures of ice which are deposited form **snow.**

On the other hand, when the weather becomes warm, evaporation goes on rapidly, especially in the neighborhood of seas, lakes, or moist country, and the proportion of water vapor in the air may be considerably *increased.*

Humidity. — The moisture is usually defined in terms of **relative humidity,** the standard being the quantity required to *saturate* the air at the existing temperature. A space filled with air can take up aqueous vapor only until the partial pressure of water vapor becomes equal to the vapor tension of water (p. 166) at the

same temperature. The humidity is then said to be 100 per cent. If the partial pressure actually reached is only half as great as the vapor tension of water at the same temperature, the humidity is 50 per cent. The average humidity may be placed very roughly at about 66 per cent.

The presence of moisture in air may be shown by placing any deliquescent (p. 213) salt, such as calcium chloride, in an open vessel. The quantity can be measured by driving a known volume of air slowly through a weighed tube containing dry calcium chloride. It may be ascertained also by noting the temperature to which the air has to be cooled before it becomes saturated and deposits fog or dew (the *dewpoint*). For example, if air at 18° has to be cooled to 11° before it deposits dew, it contains water vapor at a partial pressure of 9.8 mm. (see Appendix IV). If saturated at 18°, it would have contained water vapor under a partial pressure of 15.4 mm. Its relative humidity was therefore 9.8/15.4, or 63.6 per cent.

Moisture and Comfort. — On a moist day, we speak of the atmosphere as "heavy" or "oppressive." The barometer, however, is lower on such days, and the pressure below the average. The discomfort is due to a different cause. The chemical changes occurring in our bodies, and particularly the oxidation of waste and of digested food by oxygen carried by the blood, are accompanied by liberation of heat. Yet our bodies must remain at 98.4° F. (37° C.). A rise of a few tenths of a degree (F.) produces noticeable discomfort. Much of the heat is lost by radiation from the surface of the body. The extent of this loss depends upon the surface, which is invariable, and upon the surrounding temperature, which we cannot always control. Non-conducting clothes reduce the radiation, and are increased in thickness in cold weather. The real adjustment, however, is accomplished, independently of radiation, by evaporation of water at the surface of the skin. The evaporation of 1 gram of water at body temperature requires about 580 calories of heat. Evaporation of only 10 g. (less than half an ounce) of water will therefore lower the temperature of 58 kilograms (128 pounds) of water (or of flesh, which is largely water) by one-tenth of a degree C. (nearly 0.2° F.).

Our comfort, then, depends upon the possibility of continual, moderate evaporation from the surface of our bodies. "Much" moisture in the air means, to us, not necessarily a great absolute amount, but a near approach to the maximum possible at the existing temperature. So the ratio of the amount present to the maximum — the humidity — is the significant fact for a practical purpose, such as feeling comfortable or drying the wash quickly.

Ventilation. — In winter, cold air is brought into our rooms. The amount of water vapor contained in this air, even if it is saturated with moisture, is very small (see Appendix IV). When this air has been heated to the temperature of the room, therefore, its *relative* humidity is too low, discomfort is felt because there is too much evaporation, and moisture has to be added artificially. Here the moisture afforded by evaporation from our bodies has little effect on the air. In summer, however, the outside air is often nearly saturated at the temperature of the room. At such times the speed of displacement by the ventilating appliances may not be great enough to keep the relative humidity down, and discomfort will arise from the opposite cause. To relieve it, the evaporation may be promoted by electric fans. They do not remove or add any air, but they stir it, and blow away the moist, nearly saturated, layers next to the skin.

The chief purposes of **ventilation** are, therefore, to supply fresh air, to keep it in motion, and to maintain a humidity that is neither too low nor too high.

It should be noted that even though the air is in constant motion, the layer of air next our skin (even the exposed parts) is hindered from moving by friction. There is a **stationary layer** close to the surface, which quickly reaches the temperature of the body and becomes saturated at that temperature. The water molecules can leave this layer, and make room for others, only by *diffusion*, which is a deliberate rather than a speedy process. Now, an electric fan, although it brings no fresh, dryer air into the room, nevertheless stirs the air and blows away the moist, saturated layer next the skin. It, at least, makes this layer much thinner, and reduces greatly the distance the water molecules have to go by mere diffusion (compare p. 592).

The Carbon Dioxide. — The breathing of animals, the combustion of coal and wood, and the decay (oxidation, see p. 97) of vegetable and animal matter produce carbon dioxide CO_2. The same gas issues from volcanoes, and often in great quantities from the soil in regions which are no longer volcanic. The proportion in the air is therefore greatest in cities and in some volcanic regions, and least in the country and over the sea. It varies from 3.5 parts in 10,000 in the country to 1 per cent in crowded rooms.

The proportion of this gas in the air would naturally increase continuously, though slowly, as the result of the above processes, were it not that the gas is removed just as continuously by the action of growing plants (see p. 598), which use it as food. It may be added, also, that carbon dioxide, being a soluble gas, is contained in sea water, dissolved and as $Ca(HCO_3)_2$, and the total amount in the

ocean is much greater than that in the air. The removal by plants and by solution in sea water thus keeps the proportion in the air fairly constant.

The simplest way of showing the presence of carbon dioxide in the air is by exposing a solution of barium hydroxide, an active base, in a shallow vessel. After a short time a layer of barium carbonate forms upon the surface: $Ba(OH)_2 + CO_2 \rightarrow BaCO_3 \downarrow + H_2O$. The same action may be utilized for the purpose of quantitative analysis. A measured volume of air is bubbled slowly through a measured volume of a solution of barium hydroxide of known concentration, and the quantity of barium hydroxide remaining is determined by titration (p. 337).

The presence of carbon dioxide in the breath may be shown very quickly by blowing through a tube into calcium hydroxide solution (lime-water). Calcium carbonate $CaCO_3$ is precipitated. A candle flame is extinguished in exhaled air, because the maintenance of such a flame requires at least 18.5 per cent of oxygen. But air will sustain life until the proportion has fallen to about 10 per cent.

Carbon Dioxide and Respiration. — We draw about half a liter of air into our lungs at each breath, or half a cubic meter per hour. In the lungs some of the oxygen is removed, and some carbon dioxide is added.

	Fresh Air, Per Cent	Expired Air, Per Cent
Oxygen	21.00	15.9
Carbon dioxide	0.04	3.7

Nearly all experts are now convinced that the unhealthiness of over-crowded, "stuffy" rooms is not due to the increase in the proportion of carbon dioxide, which is seldom great enough to do any damage. Nor is it due to "poisons" given off by the lungs or skin. In spite of many experiments the presence of such substances has never been proved — they are imaginary. The harm is caused by the *stillness* of the air, which, as we have seen (p. 457), prevents the removal of the water vapor near the skin, and therefore hinders evaporation.

Dust in the Air. — A beam of sunlight crossing a dark room can be seen by the light reflected from the particles of dust which

all air contains. These are chiefly solid bodies, and are composed of salts, limestone, clay, and other rock materials, of soot and other particles of unburnt fuel, of bits of hay or straw, and of fragments of insects and other débris of plants and animals. They also include living particles, such as bacteria, and spores of plants such as moulds. The latter, when they settle upon food, germinate and give rise to putrefaction. Some of the bacteria also produce disease, when they enter the body at a place where the skin has been damaged by a cut or burn.

It is instructive to note that natural soil contains about 100,000 micro-organisms, and good, unfiltered river water from 6000 to 20,000, in each cubic centimeter. Ordinary, pure air contains only 4 to 5 micro-organisms per liter. Most of these bacteria come from the drying of soil and the dispersion of the resulting dust.

If dust were not present, we should soon notice its absence. There would be no clouds or rain. It appears that moisture will not condense to fog or rain in air which has been filtered by being drawn through a wide tube containing a long (20 inches or more) plug of cotton, and has so been freed from dust. The particles act as nuclei, round which the liquid grows at the expense of the vapor. In the absence of dust, the condensation would occur directly upon the surfaces of plants, houses, and animals. Thus, in a dustless atmosphere, an open shed or shelter, or an umbrella, would afford no protection whatever against a wetting.

The formation of fog from ordinary air, and its non-formation in filtered air are easily shown in a darkened room (Fig. 127). The flask contains water to saturate the air. When the tube leading to the water pump is opened for an instant, the saturated air in the flask expands and is cooled (see p. 460). In such circumstances, ordinary air gives a fog, brilliantly illuminated by the beam of light, while filtered air (dustless) gives none.

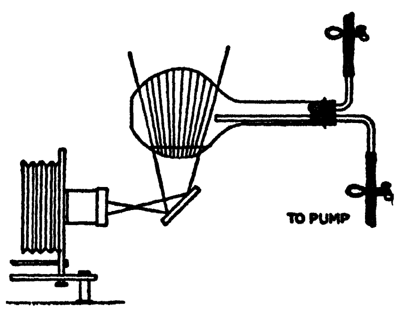


FIG. 127. Dust in the Air.

By diluting air with dustless air, generating fog in the mixture, and, with the help of a microscope, counting the globules when they settle, an estimate of the number of particles of dust in air may be made. It is found that rain removes a large proportion of them, while respiration and combustion greatly

increase their number. The prevalence of fogs in cities is thus accounted for. The following are typical numbers of dust particles in 1 c.c. of air:

Outside, raining	32,000	A room, near the ceiling	5,420,000
Outside, fair	130,000	Air above Bunsen flame	30,000,000
A room	1,860,000		

Liquefaction of Gases. — The earliest experiments of this kind seem to have been made by Northmore (1805), who liquefied chlorine, hydrogen chloride, and sulphur dioxide. In 1823 chlorine was again liquefied by Faraday; and in the same year Davy, whose assistant Faraday was, liquefied hydrogen chloride. During the following years Faraday reduced other gases — sulphur dioxide, hydrogen sulphide, carbon dioxide, nitrous oxide, cyanogen, and ammonia — to the liquid condition. He failed, however, with oxygen, hydrogen, and nitrogen.

The method which he employed was extremely simple. He used a bent tube shaped like an inverted V, into one limb of which materials for producing the gas were introduced (Fig. 101, p. 242). The other limb was then sealed up and immersed in a freezing mixture. The gas, usually liberated by heating, was liquefied by its own pressure in the cold limb. By means of a more elaborate apparatus, Cailletet and Pictet simultaneously (December, 877) obtained, the one, a fog, and the other, a spray containing droplets of liquid oxygen. In 1883 Wroblevski and Olszevski made visible amounts of the same liquid. About the same time Dewar devised means of manufacturing large quantities of liquid air and oxygen.

Liquefaction of Air. — The principle now used in liquefying gases depends on the fact that although a perfect gas, when expanding into a vacuum, should suffer no fall in temperature, since it does no work, ordinary gases at room temperatures do (with the exception of hydrogen) become cooled very slightly. The main work factor involved in expanding in such circumstances is the work done in overcoming the cohesion between the molecules (p. 123). Since this cohesion becomes more conspicuous the lower the temperature, the cooling effect of expansion becomes greater and greater as the temperature falls. At very low temperatures, even hydrogen falls into line and shows this effect.

Liquid air is now extensively prepared as a source of pure oxygen or nitrogen for use in chemical industry. The air is first freed from carbon dioxide by means of lime. It is then compressed to 200 atmospheres, the heat of compression being counterbalanced by passing through pipes cooled with running water. This compres-

sion condenses most of the water vapor present in the air, the last traces of water and of carbon dioxide being removed by solid sodium hydroxide. The air then passes into the liquefier.

In Hampson's apparatus (Fig. 128) this consists essentially of two concentric copper pipes, about 130 meters in length, coiled closely in a cylindrical form, with non-conducting covering to prevent access of heat. The compressed air is forced in through the inner pipe *A*. When it reaches the extremity of this pipe, it suddenly escapes into a closed vessel *B* through a minute opening con-

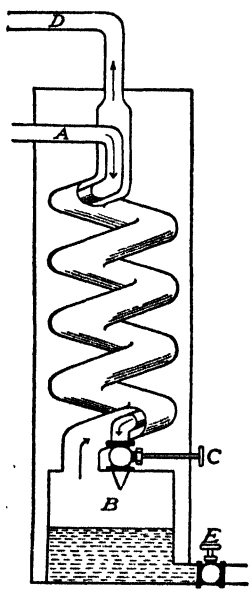


FIG. 128. Liquefaction of Air.

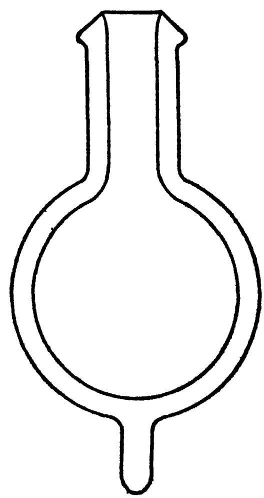


FIG. 129. Dewar Flask.

trolled by the valve *C*. This expands it to 1 atm. pressure and lowers its temperature. The air can now escape only by traveling back through the outer pipe *D* to the final exit near the top. In doing so, it cools the highly compressed air in the inner pipe. This cooler air, on reaching the closed vessel, expands and becomes colder than ever, and in passing backwards lowers the temperature of the air in the inner pipe still further. Finally, the air in this pipe liquefies, and drops of liquid air are expelled into the closed vessel. The liquid air is allowed to run out through a valve *E*, from time to time, as it accumulates.

Liquid air can be kept in Dewar flasks (Fig. 129). The space between the inner and outer flasks is evacuated, so that there is no gas to carry heat from the atmosphere in to the liquid air. The inner surface of the outer flask is often silvered, so that radiant heat, from surrounding bodies, may be reflected, and not absorbed. Similar containers are in common use for keeping liquids hot or cold for a long time (Thermos flasks).

Liquid air varies in composition, as the nitrogen (b.-p. —196°) is less condensible than the oxygen (b.-p. —182.5°). When liquid air evaporates, therefore, the first portions of gas that come off consist almost entirely of *nitrogen.* Nitrogen obtained in this way is used in the manufacture of ammonia by the Haber process (p. 508), and in the formation of calcium cyanamide (p. 734). By allowing evaporation to continue, a liquid containing 75 to 95 per cent of oxygen is obtained (compare p. 89). It contains also about 3 per cent of argon, and is a convenient source of this element. Cartridges made of granular charcoal and cotton waste, when saturated with oxygen-rich liquid air, are used as an *explosive* in mining.

Pure oxygen is more economically manufactured nowadays by means of Claude's apparatus, in which the air is liquefied in stages, two liquids, one rich in oxygen and the other in nitrogen, being obtained. The use of a long *rectifying column,* in which the escaping gas as it ascends is "scrubbed" by descending liquid, also increases the efficiency of the separation.

THE INERT GASES

Argon A. — Cavendish (1785) sought for other gases in air by adding more oxygen, passing an electric discharge to cause this gas to combine with the nitrogen, and absorbing the final product (NO_2) in potassium hydroxide solution. He found that only about 0.8 per cent of inactive gas remained. Since the quantity was so small, and the spectroscope, by which the gas even in small amounts would have been recognized to be new, was not invented until much later, he could not pursue the subject.

A century later, Lord Rayleigh observed that, while specimens of oxygen and other gases made purposely from various sources always had the same density, nitrogen was an exception. One liter of nitrogen made from the air, and supposed to be pure, weighed 1.2572 g. When the gas was manufactured by decomposition of five different compounds, such as urea and certain oxides of nitrogen, the mean weight of a liter of this nitrogen was only 1.2505 g.

The difference, amounting to nearly 7 mg., was very much greater than the experimental error. The suspicion naturally arose that some heavier gas was present in natural nitrogen. In 1894 Ramsay, in consultation with Rayleigh, succeeded in separating this gas by passing the "nitrogen" repeatedly over heated magnesium, and so removing the real nitrogen as solid magnesium nitride Mg_3N_2. The remaining gas, about 1 per cent of the whole, was named **argon** (Greek, *lazy* or *inactive*), because it would combine with no other element.

Argon has a *molecular weight* of 39.9 (nitrogen is only 28), and when liquefied *boils* at —186° and *freezes* at —189.5°. It is used in filling electric light bulbs.

Since the atomic weight of a substance is a quantity showing the proportion in which it enters into combination, it will be seen that argon, since it has not yet been found to combine with anything, has, to speak strictly, no atomic weight (pp. 185–8).* At the same time, it is manifestly a question of interest to determine whether the physical properties require the supposition that the molecule of argon contains one atom, or more than one atom.

If gases were composed of perfectly elastic spheres, the molecules would be altered only in respect to velocity of movement by heating. Calculation enables us to determine that to raise the temperature of one G.M.V. of *such a gas* by one degree would require 3 calories in every case. Now Regnault found the following values (in calories) for the heat capacity of gases at constant volume:

Oxygen (O_2)	4.96	Carbon dioxide (CO_2)	7.56
Hydrogen (H_2)	4.82	Sulphur dioxide (SO_2)	7.82
Nitrogen (N_2)	4.82	Chloroform ($CHCl_3$)	16.55
Hydrogen chloride (HCl)	4.76	Alcohol (C_2H_6O)	18.70

These gases evidently are not constituted as the above-mentioned hypothesis supposes. Some heat is consumed in work done *inside* the polyatomic molecules, and the amounts by which the numbers exceed 3 calories show that the intramolecular work is greater as the complexity of the molecules increases. Now in mercury vapor the value is exactly 3, and its vapor is monatomic (p. 796), so that in its molecules there is no opportunity for the consumption of heat in intramolecular change. Hence, when argon was found likewise to give 3 for the value of its molecular heat-capacity, identity of its atomic and molecular weights was demonstrated.

Helium He. — In 1868 Lockyer first detected an orange line in the spectrum of the sun's prominences which was not given by any terrestrial substance then known. The line was so conspicuous that it was attributed to the presence of a new chemical element, which

* Argon and the other inert gases do possess, however, *atomic masses*, as will appear in the following chapter (p. 477).

was named **helium** (Greek, *the sun*). Ramsay, in searching for sources of argon, examined a gas which Hillebrand had obtained from uraninite, an ore of uranium. He was surprised to find (1895) that it contained a large proportion of a very light gas, the spectrum of which was identical with that of solar helium.

The *molecular weight* of helium is 4.00, so that it is only twice as dense as hydrogen. It was the last gas to be liquefied (by Onnes); the liquid *boils* at —268.7° (4.3° Abs.) and *freezes* below 1° Abs. Like argon, it does not enter into chemical combination. This very unsociability of helium, however, renders it the ideal gas for airships and avoids all the risk of fire or explosion attendant upon the use of hydrogen. Helium is also now being used to replace the nitrogen in the compressed air supplied to workmen engaged in caisson work, *e.g.*, in tunneling under rivers. It has been found that the lower solubility of helium in water greatly reduces the danger of such workmen suffering from "bends" (release of air bubbles in the blood, frequently with fatal consequences) on returning to the surface. Helium exists in small quantity in many natural gases (see p. 580), and is obtained pure by liquefying out the other components.

Other Inert Gases. — When liquefied argon was allowed to evaporate, the first vapor coming off was found to contain another gas, **neon** (Greek, *new;* mol. wt. 20.2), along with helium. Careful fractional distillation of the residual liquid (see under Petroleum, p. 579) gave two other gases, **krypton** (Greek, *hidden;* mol. wt. 83.7) and **xenon** (Greek, *stranger;* mol. wt. 131.3). The relative amounts of these four gases in the air, however, is very small compared with argon, the volume percentages running as follows: argon 0.9323; neon 0.0015; helium 0.0005; krypton 0.0001; xenon 0.00001. The penetrating orange-red glow which is obtained when an electric discharge is passed through a vacuum tube containing traces of neon is now utilized in electric signs and in beacons for aviation fields.

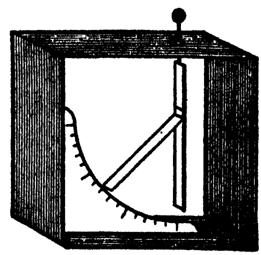
None of these gases forms any compounds. They do not combine with themselves even, as do the more common gases such as H_2, O_2, Cl_2. The molecule in each case is *monatomic,* for example Ne, Kr, Xe. The **valence** throughout the group is therefore **zero** (see p. 444).

Radon (radium emanation; see p. 466), with a molecular weight of 222, also belongs to the family of inert gases. This gas is employed in hospitals in the treatment of superficial cancerous

growths. Its mention at this appropriate point leads us on to a detailed discussion of the phenomena of **radioactivity.**

RADIOACTIVITY

The Discovery of Radium. — In 1896 Henri Becquerel discovered that a crystal of a salt of uranium could, in the dark, reduce the silver bromide on a photographic plate, even when a sheet of black paper (impervious to light) was placed between. Evidently a *radiation,* different from light, was given out by the salt. Next he discovered that an electrometer (Fig. 130), in which the gold leaves had been caused to separate by charging with electricity, lost its charge rapidly when a salt of uranium was brought near to the knob connected with the leaves. Evidently the salt *rendered the air a conductor* ("ionized" the air), and this permitted the escape of the electricity.


FIG. 130. Electrometer.

The "radioactivity" of every pure uranium compound is proportional to its uranium content. The ores are, however, relatively four times as active. This fact led M. and Mme. Curie, just after 1896, to the discovery that the pitchblende residues, from which practically all of the uranium had been extracted, exhibited nevertheless considerable radioactivity. About a ton of the very complex residues having been separated laboriously into the components, it was found that a large part of the radioactivity remained with the sulphate of barium. From this a product free from barium, and at least one million times more active than uranium, was finally secured in the form of the bromide. The nature of the spectrum and the chemical relations of the element, now named **radium,** placed it with the metals of the alkaline earths (see p. 720).

In 1910 Mme. Curie obtained metallic radium by electrolyzing a solution of radium chloride, using a mercury cathode, and expelling the mercury by distillation. It was found to be a white metal (m.-p. 700°) which like calcium, quickly tarnished in the air and displaced hydrogen from water.

The Nature of the "Rays." — The "rays" emitted by compounds of uranium and of radium are of three kinds. They are most sharply distinguished from one another when allowed to pass through a powerful magnetic field (Fig. 131). The **alpha-rays** are positively charged and are bent in one direction while the

beta-rays are negative and are bent in the other. The **gamma-rays** are not affected.

The *alpha-rays* are **atoms of helium** (p. 464) thrown off in straight lines with varying initial velocities, depending upon the radioactive element employed, but averaging about one-tenth that of light. Each such atom bears a **double positive charge** (in other words, it has *lost two electrons,* see p. 69).

The *beta-rays* are **electrons** (p. 63), or unit charges of negative electricity, and are shot out with a velocity approaching that of light (300,000 kilometers per sec.).

The *gamma-rays* are identical with X-rays (see p. 63), and are presumably produced like the latter by the impacts of the electrons on the surrounding matter.

The helium atoms are almost all stopped by a sheet of paper or by aluminium foil 0.1 mm. thick. The electrons have greater penetrating power, many passing through gold-leaf, but being practically all blocked by a sheet of aluminium 1 cm. thick. The gamma-rays (X-rays), however, are able to penetrate relatively thick layers of metals and other materials of low atomic weight.

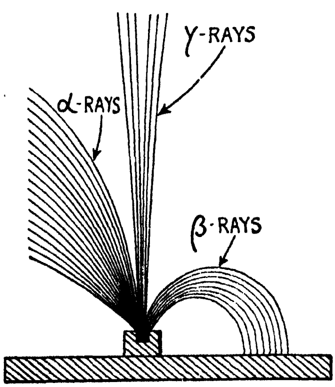


FIG. 131. Action of a Magnetic Field on Alpha-, Beta- and Gamma-Rays.

The emission of atoms of helium can be detected by means of Crookes' spinthariscope (Fig. 132). The sample of radium bromide is at *B,* and some of the ejected helium atoms strike a surface *C* covered with zinc sulphide, producing faint flashes of light. The lens *A* magnifies the flashes, which can be seen in a dark room after the eye has become thoroughly rested (15–20 minutes). The helium gas given off by radium compounds was collected by Soddy (working with Ramsay) and identified, and its rate of production was measured. The amount was equal to 158 cubic mm. per 1 g. of radium per year.

Disintegration. — The emission of atoms of helium and of electrons was first explained by Rutherford (1902–3), then of McGill University, Montreal, as being due to the **spontaneous disintegration of the atoms of uranium, radium, and other radioactive elements.** Thus, Rutherford was the first to show that radium compounds produced a gaseous substance called the radium emanation **(radon),**

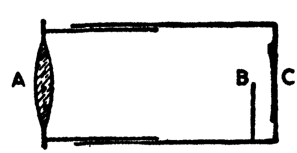


FIG. 132. Crookes' Spinthariscope.

which was the residue left after the emission of one atom of helium from an atom of radium. This gas was itself radioactive and underwent further disintegration, depositing a solid radioactive residue on bodies in contact with it. Furthermore, every known uranium ore contains radium and radium emanation in amounts proportional to the uranium content. It thus appears that uranium is the starting point, and that the disintegration proceeds by steps, producing a number of different products. Each of these is formed from one such product and by disintegration furnishes another.

Unlike ordinary chemical change, the rate of disintegration is not affected by conditions. It can neither be started nor stopped at will. It is no more vigorous at a white heat than at the temperature of liquid air. Other changes occur between atoms, these within each atom.

The law, due also to Rutherford, describing the rate at which any one radioactive element disintegrates, is simple. Only a certain fraction of the whole of any one specimen undergoes the change in unit time. Thus, as the total amount diminishes because of the change, the amount changing during the next unit of time, being a constant fraction of the whole, must be less. Hence an infinite time would be required for the complete disintegration of any one specimen. For convenience, therefore, it is usually the custom to give as a specific property of each radioactive element its **half period,** or the time required for the decay of half its amount and therefore the loss of half of its radioactivity.

Radium emits helium atoms at the rate of 3.4×10^{10} per gram per second. From this fact, we can calculate its half period to be about 1700 years. Hence, if it were not continuously being produced (from uranium), the whole supply would have been exhausted long before the earth reached a habitable condition.

The Uranium Group of Radioactive Elements. — The following table shows the various elements produced from uranium by successive disintegrations. When a helium atom or an electron is expelled, the fact is shown by the symbols He and ϵ, respectively. The first number below each element is the half period of that member of the series (y = year, d = day, h = hour, m = minute, s = second). The second number is the atomic weight, obtained by subtracting from the at. wt. of uranium (238) the weight (4) of each helium atom emitted.

The radium emanation was shown by Ramsay to be one of the inert gases (p. 464). Ramsay called it *niton,* but it has recently been renamed **radon,** to indicate its source. Its density was determined experimentally with a small sample, using a micro-balance

capable of weighing 1/500,000 mgm., and found to be 222 (density of oxygen = 32).

The end-product of the disintegration is **lead,** and all uranium ores contain lead (see p. 43).

U_1	→	He + U-X_1	→	ϵ + U-X_2	→	ϵ + U_2	→	He + Ionium
4.67×10^9 y.		24.6 d.		1.15 m.		2×10^6 y.		6.9×10^4 y.
238		234		234		234		230
→ He + Ra	→	He + Radon	→	He + Ra-A	→	He + Ra-B		
1690 y.		3.85 d.		3.0 m.		26.8 m.		
226		222		218		214		
→ ϵ + Ra-C	→	ϵ + Ra-C_1	→	He + Ra-D	→	ϵ + Ra-E		
19.5 m.		10^{-6} s.		16.5 y.		5.0 d.		
214		214		210		210		
→ ϵ + Ra-F	→	He + Pb (end)						
136 d.		Infinity						
210		206						

Thorium, found as phosphate in monazite sand, is also radioactive and furnishes a similar series of disintegration products. The final material is again **lead.**

Actinium forms one step of a third series of radioactive elements, which have not yet been fully investigated. Compounds of potassium and rubidium show traces of radioactivity.

Chemical Actions of the "Rays." — The radiations which are most active in ionizing air and in acting upon photographic plates are the α-particles. These particles also cause the flashes of light when they encounter zinc sulphide. The radiations change the colors of minerals, including gems, and give a deep violet color to the glass tube containing the specimen. They also turn atmospheric oxygen in part into ozone and, in solution, produce traces of hydrogen peroxide in the water.

The radiations destroy minute organisms and kill the cells of the skin, producing sores. They have been employed in the treatment of lupus and of superficial cancerous growths.

Transmutation of Elements; Atomic Energy. — The phenomena of radioactivity establish the transmutation of elements, long regarded as a delusion of the alchemists, as an indisputable fact. Artificial means of disintegrating the more common elements, even, have recently been devised (see pp. 25, 484), but thus far only on an exceedingly small scale. We cannot control in any way the *rate* of disintegration of radioactive elements (see p. 467). If, however, some method of inducing or hastening radioactive changes on a large scale is discovered in the future, a wonderful new source of power will be put into our hands, namely, **atomic energy.**

The energy change in radioactive disintegrations is enormously greater than in ordinary chemical reactions. One gram of radium, undergoing spontaneous disintegration, would evolve about 120 calories per hour, and would continue to evolve this heat, at a gradually decreasing rate, for centuries. The total heat available would be over 2,000,000,000 calories per gram, whereas a gram of carbon burning to CO_2 gives only 8070 calories (p. 260). The disintegration of a pound of uranium salts would furnish enough power to drive an ocean liner across the Atlantic, but 5,000,000,000 years is entirely too long to wait for the completion of the trip. Chemists are already visualizing, however, the possibility of using the enormous stores of energy here available so soon as a *catalyst* for the reaction is obtained.

Another interesting by-product of this subject is the calculation that the heat given off by the disintegration of the radioactive elements existent in the earth (radon is found in small quantity in the soil and in well waters) is sufficient *alone* amply to account for the maintenance of its temperature. A globe the size of the earth, possessing originally only heat energy, and cooling from a white-hot condition to the temperature of interstellar space, would have passed through the stage of habitable temperatures in a much shorter time than that which geological deposits and fossils show to have actually elapsed. The discovery of the enormous, but gradually released, disintegration energy of elements such as radium, enables us now to explain the prolonged period during which life has existed on the earth.

Exercises. — 1. Does the removal of oxygen from air by means of heated mercury (p. 88) prove that air is a mixture?

2. At 77° F. the air of a room contains water vapor at a partial pressure of 20 mm. What is the percentage humidity?

3. What weight of water is contained in a cubic meter (1000 liters) of air saturated at 10° C.?

4. Air at 18° has to be cooled to 14° before it deposits dew or fog. What is the percentage humidity?

5. Why is the air nearest the ground heated (by the sun) to a higher temperature than the upper air?

6. Formulate a method for the complete *quantitative* analysis of air.

7. A sample of moist air, confined over water at 15° and 760 mm., occupies 15 c.c. It is mixed with 20 c.c. of hydrogen, and the mixture is exploded, and suffers a contraction of 9.5 c.c. What would be the volume of the oxygen it contained if measured dry at 0° and 760 mm.?

8. What is the weight of argon present in an "empty" room, measuring $10 \times 10 \times 5$ meters, at 20° and 1 atmosphere pressure (p. 464)?

9. Xenon exists in air only in the proportions of 1 part in 170 millions by volume? How many atoms of xenon are there in 1 c.c. of air at 0° and 760 mm.?

10. What are the relative lifting powers of hydrogen and helium, as used in balloons? Neglect the weight of the balloon itself.

11. Lord Rayleigh found (p. 462) that one liter of atmospheric "nitrogen" under standard conditions weighed 1.2572 g., while one liter of really pure nitrogen weighed only 1.2505 g. Assuming the impurity in the former sample to be entirely argon, with an atomic weight of 39.9, calculate from the above data the volume of argon in 1 liter of atmospheric "nitrogen."

12. From the position of radium in the periodic system, predict (using the table on the Inside Cover as a guide) the approximate molar solubilities of the chief salts of radium in water at 18°.

13. A careful analysis of pure radium chloride showed that the chlorine in 0.60385 g. $RaCl_2$ was equivalent to that in 0.58316 g. AgCl. What is the atomic weight of radium?

14. Ramsay and Gray, working with a microbalance on the atomic weight of radon (radium emanation), found that 0.0730 cubic centimeter of the gas at 0° and 760 mm. weighed 0.710 milligram. What is the atomic weight of radon (see p. 468) indicated by this result?

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CHAPTER XXVII

ATOMIC NUMBERS AND ISOTOPES

In this, and in the next, chapter an effort is made to indicate some of the more significant recent advances in our knowledge of the fundamental principles of chemistry. The topics taken up are presented in the briefest possible outline, and it is not expected that the beginner will derive, from these pages alone, anything more than a general idea of the trend of modern chemical theory. How revolutionary this has become may be recognized by the jocular proposal that the Atom (Greek, *a-* not, *-tom* divided; see p. 55) be now rechristened "Tom" to celebrate its dismemberment.

Fascinating as the results of recent work may appear, the reader should not lose sight of the fact that, for all practical purposes and in the chemistry of daily life, the immutability of elements, the constancy of atomic weights, and the law of definite proportions may still be accepted and utilized without any reservations.

The Constitution of Matter. — From very early times, it has been a favorite speculation of philosophers that all matter could finally be reduced, by ultimate analysis, to one primary substance. At various periods, Fire, Water, Earth and Air have been suggested as this hypothetical original source of all materials. This belief persisted, with various modifications, through the period of the alchemists, whose chief problem lay in the attempted discovery of methods of transmutation.

The development of the idea of specific elements and the general acceptance of the atomic theory of Dalton did not entirely displace this conception of a final parent substance. In 1815, Prout put forward a definite hypothesis that the atoms of all elements were more or less complex aggregates of atoms of hydrogen. According to this view, the atomic weights should evidently all be expressed by integral numbers on the basis $H = 1$. At that time, accurate atomic weight determinations were very few in number, and among the common elements there are so many with atomic

weights which are remarkably near to whole numbers (compare p. 56) that a great many chemists were disposed to accept Prout's hypothesis as correct. As more exact analytical methods were developed, however, the invalidity of the hypothesis gradually became evident, and in 1860 Stas, who had himself redetermined many atomic weights with the greatest possible refinement of method and apparatus, apparently wrote the doom of the theory in the following words: "I have arrived at the absolute conviction, the complete certainty, so far as it is possible for a human being to attain to certainty in such matters, that the law of Prout is nothing but an illusion, a mere speculation definitely contradicted by experience."

The change to the scale $O = 16$, however, brought the question before chemists once more. While it is perfectly true that a great many of the atomic weights on this scale are far removed from whole numbers, yet it is extraordinary how large a proportion of the common elements possess atomic weights which lie very close indeed to simple integers. Mention may be made of carbon, 12.00; nitrogen 14.008; and sodium 22.997 as examples. The number of such elements is much greater on the scale $O = 16$ than on the scale $H = 1$. This congregation of atomic weights around simple integral numbers may, of course, be due merely to chance, but Sir William Ramsay, from an examination of the whole list of elements, arrived at the conclusion that the odds were many billions to one against so many atomic weights being *fortuitously* such close approximations to integers.

Electrons and Protons. — The discovery of the electron and the study of radioactivity finally indicated the solution of the difficulty. It was shown by Sir J. J. Thomson that the β-ray or **electron** (the unit of negative electricity) was the same, whatever element it sprang from; its electrical charge being 4.774×10^{-10} electrostatic units and its mass 0.00054 on the ordinary scale of atomic weights ($O = 16$). Evidence has quite recently (1933) been obtained of the existence of "positively-charged electrons," or **positrons,** with the same mass but with equal and opposite charge. Positive electrons, however, are at present of interest solely to the physicist, since they possess only the most transient existence. On the chemical side, the positively-charged particle of smallest mass that demands practical consideration is *the hydrogen atom which has lost an electron.* This particle, which has been called the **proton,** is possibly itself complex in its constitution (see p. 479), but may be regarded, for the present, as our *unit of positive electricity.*

Its charge, of course, is equal and opposite to that of the electron, and its mass has been shown by direct measurement to be 1.0073 on the oxygen scale.

The possibility that the atoms of all elements might be built up of aggregates of protons and electrons has led to a tremendous amount of research work on all aspects of the problem. Sir Ernest (now Lord) Rutherford first formulated in 1911 a number of principles regarding atomic structure which still constitute the basis of current theory. The atom of any element was postulated as consisting of a very minute central nucleus, positively charged, surrounded by planetary electrons. These planetary electrons are at relatively large distances from the nucleus, just as the planets are at relatively large distances from the sun in our solar system. The central nucleus contains *all* the positive electrical units or *protons*, and is consequently responsible for practically the entire mass of the atom. The external electrons, on the other hand, are responsible for practically the entire volume occupied by the atom. Only in radioactive transformations does the nucleus change; ordinary chemical reactions affect merely the external electrons.

With this model as a basis, the most wonderful advances ever made in the history of the science have resulted during the last twenty years. For a time the difficulty of fractional atomic weights was disregarded, since such rapid strides were being made in other lines, but now a complete explanation of this point has also been obtained. The first important conception introduced, however, was Moseley's **atomic numbers.**

Atomic Numbers. — We have already discussed in a preceding chapter (p. 64) how X-rays may be used to analyze the arrangement of atoms in crystals. The fact that the atoms in crystals act as a diffraction grating for X-rays may be utilized also in the reverse direction. We may fit an X-ray spectroscope with an analyzer consisting of a reflecting crystal, and so obtain a spectrum of the radiation in which each line corresponds to a definite wavelength. The principle is just the same as the analysis of white light by the common prism, or the production of the characteristic spectrum of a metal like potassium in the ordinary spectroscope (see p. 706). It has the advantage, however, that the lines obtained with X-rays from a definite source are very few in number.

As we have seen, X-rays are produced in an evacuated tube (Fig. 29), through which an electrical discharge is passed, when the streams of electrons emanating from the cathode (cathode rays)

strike the anti-cathode. With different elements on the anti-cathode, X-rays of slightly different wave-lengths, and therefore giving different X-ray spectra, are produced. The characteristic radiations for each element appear in two distinct series, known as the K (hard) and L (soft) series, but each series is made up of a strong line and a weaker one a little distance from it, as shown in Fig. 133 for a series of successive elements in the Mendelejeff periodic table (p. 446), ranging from titanium to copper. There is evidently some simple connection between the position of these lines and the position of the element in the periodic system, but if we attempt to correlate the wave-lengths of the lines with the *atomic weights* of the elements, we run at once into difficulties. This will be immediately evident from the fact that the atomic weights of nickel and of cobalt are in the wrong order, whereas their spectra step up uniformly with those of the other elements.

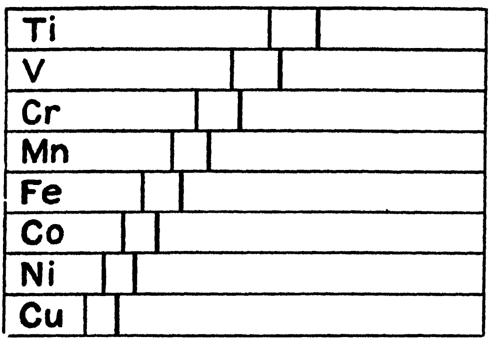


FIG. 133. K Series of X-ray Spectra (diagrammatic only).

Atomic weights, then, which show *very divergent* intervals between successive elements, are not of service in elucidating the *regular* variation in the position of the X-ray spectra. This variation, however, may be demonstrated theoretically to be directly related to **atomic structure,** the rule being that the greater the number of free protons (unit positive charges) in the nucleus of the atom, the shorter should be the wave-length of the characteristic X-rays. It was shown by Moseley (a brilliant young English physicist, killed at Gallipoli) that when successive elements are arranged in the order of these wave-lengths, successive **whole numbers** can be assigned to each which are inversely proportional to the square roots of the wave-lengths of corresponding lines in their X-ray spectra (see Fig. 134). These **atomic numbers** have been directly determined for most of the elements, the atomic weights of which lie between those of sodium and uranium, by the method discussed above. In the following table, the atomic numbers thus found for these elements are given and, for completeness, numbers

constitution of its atom with those of more complex structure. The minute nucleus of the hydrogen atom consists of a solitary proton, and the single external electron is, relatively, at an enormous distance therefrom. An analogy may make this clearer. Imagine a hydrogen atom magnified until it became as big as the Yale Bowl. The nucleus would then be equivalent in size to a golf ball in the center, while the electron might be represented by a man in an aëroplane circling over the outermost ring of seats.

In all other atoms, on the contrary, we have proton-electron pairs congregated in close proximity in the almost inconceivably restricted space occupied by the nucleus. The important question arises: Will the mass of a proton-electron pair packed into such a narrow compass be the same as when the partners are widely separated?

Leaving the theoretical implications of this question for consideration in the following section, we may give here an immediate experimental answer. The element beryllium, when bombarded by alpha-particles, was found to emit not hydrogen-ions as in the case of other light elements (see pp. 25, 484), but a very penetrating radiation which, on careful examination, was shown to consist of "collapsed hydrogen atoms," or pairs of embedded protons and electrons. These particles have been named **neutrons,** and their mass is *not* equal to that of the hydrogen atom. The most probable value as at present determined is 1.006.*

The neutron may be considered as the element with atomic number *zero,* since its nucleus contains no free proton. The alternative possibility exists, however, it must be noted, that the neutron is a fundamental non-electrical unit of mass, and that the proton consists of the union of a neutron with a positron (p. 472). Similar the electron may be regarded as the element with atomic number *minus one.*

The Packing Effect: Hydrogen and Helium. — The change in the mass of a proton-electron pair brought about by bringing them together has been called the **packing effect.** This effect is still more pronounced in the atoms of heavier elements — where several or many pairs (with several or many excess protons) are compressed into the nucleus — than in the simple neutron. This may be seen by examining the element with atomic number two — **helium.**

The helium atom (p. 487) consists of two exterior electrons, two free protons in the nucleus and two embedded proton-electron pairs. The helium atom therefore contains the same material as four hy-

* More recent measurements suggest a higher value (1.0085).

drogen atoms, *arranged in a different way*. But the mass of the helium atom is not $4 \times 1.0078 = 4.0312$; it is 4.002. By rearrangeing our protons and electrons we have lost almost 0.03 units of mass. How is this possible?

The answer is: *What we have lost in mass, we have gained in energy*. The fact that all matter has an ultimate electrical structure (protons and electrons) forces us to conclude that matter and energy are not distinct phenomena, but interchangeable. Matter is potential energy; energy is potential matter. The law of conservation of mass holds within our limits of weighing, for all ordinary chemical reactions, only because the energy changes involved are extremely small. But radioactive disintegrations have already demonstrated to us that energy changes in reactions "within the atom" may be enormously great. Correlating our laws of conservation of mass and conservation of energy into one wider law — **conservation of mass-energy** — we can calculate what change in mass corresponds to any particular energy change, and *vice versa*. We find that the mass change in all ordinary chemical reactions is infinitesimal, and that even in radioactive disintegrations it is exceedingly minute. Conversely, if the mass change is appreciable, as in the case of hydrogen-helium, the energy change involved in the re-arrangement of the protons and electrons must be stupendously large. The conversion of 1 gram of hydrogen to helium, indeed, would liberate energy equivalent to (in terms of heat) 166,000,000,000 calories or (in terms of work) 200,000 kilowatt hours.

Here at last is a source of energy sufficient to account for the heat of the sun, and if this tremendously exothermal reaction, once started, were to run out of control and proceed explosively, all of the hydrogen on the earth might be transformed at once and the success of the experiment signalled to the rest of the universe as a new and exceedingly bright star!

Fortunately, it is not very likely (see p. 485) that this will occur in the near future.

The Packing Effect: Heavier Elements. — The packing effect is also significant in the elements succeeding helium in the periodic table. Its proportionate influence on atomic mass as we ascend the series becomes, after a time, *almost constant*, but not exactly so. This may be best illustrated by comparing all atomic masses with that of the mass-spectrograph standard, O^{16} (see Fig. 136). The horizontal scale in this diagram represents the mass number, *i.e.*, the total number of protons in the nucleus. The vertical scale shows the percentage difference between the mass of each atom

and its mass number — a quantity which Aston has named the **packing fraction.** The packing fraction expresses the mean gain or loss in mass per proton when the nuclear packing is changed from that of O^{16} to that of each atomic species shown in the figure. As the curve demonstrates, it varies in a regular way throughout the whole list of elements, the only complication being a split into two distinct branches for the lighter elements. These branches follow the elements of odd and even atomic number respectively.

Several points of interest emerge from this curve. The initial, steeply-descending sections indicate that the masses of atoms lighter than O^{16} are slightly *higher* than whole numbers on the standard

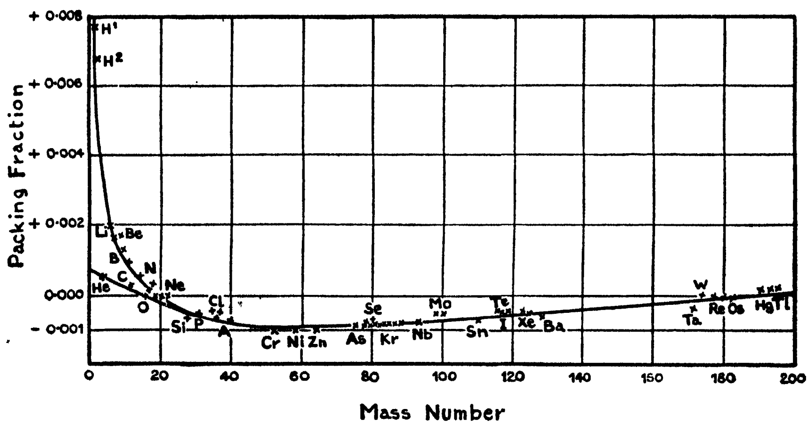


FIG. 136. Variation of Packing Effect with Atomic Mass.

scale $O^{16} = 16$. From fluorine 19 to mercury 200 (approximately) the packing fraction is negative, so that atomic masses in this interval are slightly *lower* than whole numbers. Above mercury, the curve crosses the zero line once more, and atomic masses are again slightly *above* integral values.

It is significant, furthermore, that the *minimum* in the packing fraction lies in the region of *iron,* one of the most abundant elements in nature (the chief component of the interior of the earth and of meteorites). From energy considerations, atoms in the neighborhood of this minimum point should be the most stable, whereas at the two extremes highly exothermic transformations to other types are possible. For the lightest atoms these transformations would be in the direction of heavier products (*e.g.*, hydrogen → helium, as discussed in the preceding section). For the heaviest

atoms, on the contrary, they would be in the direction of lighter products (*e.g.*, the uranium disintegration series, p. 468). Elements with a higher atomic weight than uranium are presumably too unstable to exist at all.

The delicacy of Aston's mass-spectrograph method has now been developed to such an extreme that his latest results give "physical values" for atomic masses accurate, in most cases, to more places of decimals than the old "chemical values" for atomic weights. Since the relative abundance of the isotopes may also be estimated, within very narrow error limits, by mass-ray analysis, it is evidently possible to check chemical atomic weights by purely physical means. In several instances, indeed, where discrepancies have been discovered, careful investigation has shown that the accepted chemical values are at fault and require more exact redetermination. A single illustration of a simple type may be given. Phosphorus (chemical atomic weight, 31.02) has no isotopes, the only atomic species found on the mass-spectrograph possessing a mass number of 31. The packing fraction of phosphorus, however, is *negative,* so that its true atomic weight should be slightly *less,* not slightly *higher,* than 31. The actual value deduced by Aston was 30.978, and a recent determination of the atomic weight of phosphorus from the limiting density of phosphine PH_3 by Ritchie gave 30.977, in striking agreement with this.

Isotopes of Oxygen and Hydrogen.—Until 1929, physical atomic weights (based on the O^{16} line in mass-spectrograph determinations) and chemical atomic weights (based on oxygen = 16) were regarded as absolutely identical. Not only did the mass-spectrograph give no indications of the existence of any isotopes of oxygen, but the hydrogen : oxygen ratio on the physical scale was exactly the same (1.00778 : 16) as on the chemical scale. From band-spectra analysis, however, Giauque and Johnston obtained unambiguous proof of the existence of minute traces of O^{18}, and still more minute amounts of O^{17}, in ordinary oxygen. Similarly, traces of C^{13} were found in carbon and traces of N^{15} in nitrogen.

The exact concordance between the hydrogen : oxygen ratio on the two scales was thus disturbed, and although the discrepancy amounted to *only one-fiftieth of one per cent* this was sufficient to induce chemists to postulate the existence of a heavy isotope of hydrogen in quantity sufficient to restore the balance. In 1932, spectroscopic evidence of H^2 was obtained by Urey, Brickwedde and Murphy. This "heavy hydrogen" has a mass of 2.0136, and

constitutes about one part in six thousand of ordinary hydrogen. For reasons which will appear below, it has been distinguished by a separate name, **deuterium,** and a separate symbol, D. The isotope H^3 (**tritium**) has also been found to exist, but in almost infinitesimal quantity.

Deuterium and "Heavy Water." — In view of the identity of chemical properties exhibited by the isotopes of other elements (see p. 478), it would appear at first sight very unlikely that deuterium could be readily isolated in a pure state, or that its compounds would be materially different from those of ordinary hydrogen. But the similarity between the isotopes of hydrogen is by no means comparable with the similarity between the isotopes of heavier elements, say the two isotopes of chlorine. The new variety of hydrogen atom comprises a nucleus of one free proton and one proton-electron pair, with one external electron. Not only is its nucleus twice as massive as that of ordinary hydrogen, whereas the difference between the two chlorine nuclei is only a small fraction, but this nucleus is also — particularly in the polar compounds of hydrogen where the single protecting electron migrates away — practically naked, whereas the nuclei of chlorine are wrapped around with successive and similar shells (see pp. 493–8).

While, therefore, many years' work on the separation of the isotopes of chlorine by Harkins merely resulted in a very meagre fractionation, success in the separation of the two types of hydrogen has been rapid and complete. The most striking results have been obtained by Lewis, who by a series of fractional electrolyses of a solution of sodium hydroxide has obtained a residue of pure "heavy water" D_2O — water in which all the hydrogen is in the form of the heavy isotope with mass 2. Since the study of the properties of this substance is still in its infancy, we shall restrict ourselves here to mentioning its salient differences from ordinary water. Its density is more than ten per cent higher, it freezes at + 3.8° C., it boils at 101.6° C., and it has a maximum density at 11.6° C.

A few remarks about its biological behavior, however, must be appended. Tobacco seeds will not germinate in pure heavy water, and the life processes of plants in diluted heavy water appear to be considerably retarded. Pure heavy water has also been shown to be toxic to various species of animal life, such as tadpoles and flatworms. What its effect upon the human organism may be

is at present only a matter of interesting speculation; it is quite possible that it may turn out to be of immense importance in medicine.

Artificial Transmutation of Elements. — We shall close this chapter by a brief discussion of the transmutations obtained by Rutherford and others as the result of atomic bombardments.

It has already been mentioned (p. 25) that when certain light elements, such as nitrogen and aluminium, are bombarded by *alpha-particles* (helium atoms), hydrogen is one of the products. The complete equations may now be written:

$$_{7}N^{14} + {}_{2}He^{4} \rightarrow {}_{8}O^{17} + {}_{1}H^{1}$$
$$_{13}Al^{27} + {}_{2}He^{4} \rightarrow {}_{14}Si^{30} + {}_{1}H^{1}.$$

The subscript before the symbol in each case indicates the atomic number. We see that these are examples of the artificial building up of heavier elements from lighter ones. Similarly when beryllium is bombarded by alpha-particles (p. 479) we have the reaction:

$$_{4}Be^{9} + {}_{2}He^{4} \rightarrow {}_{6}C^{12} + {}_{0}n^{1}.$$

The symbol n here denotes the collapsed hydrogen atom, or neutron, with atomic number zero and mass 1.

When lithium is bombarded by *protons,* two reactions occur:

$$_{3}Li^{6} + {}_{1}H^{1} \rightarrow {}_{2}He^{4} + {}_{2}He^{3}$$
$$_{3}Li^{7} + {}_{1}H^{1} \rightarrow {}_{2}He^{4} + {}_{2}He^{4}.$$

Similarly, when lithium is bombarded by *deutons* (deuterium nuclei):

$$_{3}Li^{6} + {}_{1}D^{2} \rightarrow {}_{2}He^{4} + {}_{2}He^{4}$$
$$_{3}Li^{7} + {}_{1}D^{2} \rightarrow {}_{2}He^{4} + {}_{2}He^{4} + {}_{0}n^{1}.$$

And finally, when nitrogen is bombarded by *neutrons:*

$$_{7}N^{14} + {}_{0}n^{1} \rightarrow {}_{5}B^{11} + {}_{2}He^{4}.$$

These examples of the artificial disintegration of heavier elements to lighter ones will suffice to show how widely we have departed in recent years from Dalton's atomic theory. Nevertheless, the statements made at the beginning of this chapter may here be

repeated for emphasis: For all practical purposes and in the chemistry of daily life, the immutability of elements, the constancy of atomic weights, and the law of definite proportions may still be accepted and utilized without any reservations.

The possibility of utilizing artificial transmutations as a source of atomic energy is exceedingly remote. It is true that the hydrogen nuclei resulting from the bombardment of aluminium atoms by alpha-particles possess more energy than the original alpha-particles, but only about two alpha-particles in a million succeed in effecting the liberation of hydrogen from aluminium. In view of what has been said in a previous section (p. 479) regarding the minute size of the atomic nucleus, the difficulty of scoring a direct hit thereon will be obvious. This difficulty is increased, as the atomic number of the bombarded atom is raised, by the deflecting action of the cloud of exterior electrons surrounding the nucleus, and heavy elements such as gold are accordingly found to be quite insensitive to most atomic bombardments.

Neutrons, nevertheless, penetrate the exterior electron shells quite readily, and it has even been claimed recently that elements with atomic number higher than 92 are obtained by the neutron bombardment of uranium.

Induced Radioactivity.—In 1934, I. Curie (daughter of Mme. Curie) and F. Joliot observed that when boron was bombarded with alpha-particles from polonium, positrons were emitted in large numbers, and this emission of positrons did not cease immediately the source of the bombardment was withdrawn. It continued instead for some time, decaying slowly just as in the case of a radioactive element, the half-period being 14 minutes. This could only be explained by assuming that new atomic nuclei had been created by the interaction of alpha-particles with boron atoms, and that these new nuclei were undergoing spontaneous disintegration.

Curie and Joliot ascribed the induced radioactivity of boron in the above experiment to *radioactive nitrogen* N^{13}, an isotope not known in nature but formed by the reaction:

$$_{5}B^{10} + {}_{2}He^{4} \rightarrow {}_{7}N^{13} + {}_{0}n^{1}$$

and subsequently disintegrating as follows:

$$_{7}N^{13} \rightarrow {}_{6}C^{13} + {}_{1}\epsilon^{+}$$

They predicted that this same N^{13} would be produced by the bombardment of carbon by deutons:

$$_{6}C^{12} + {}_{1}D^{2} \rightarrow {}_{7}N^{13} + {}_{0}n^{1}$$

and this prediction was shortly afterwards confirmed. Since then, a multitude of radioactive isotopes of familiar elements have been obtained by various types of atomic bombardment, and their half-periods determined. Radio-sodium, Na^{24}, for example, has a half-period of 15.5 hours. It has already been produced in quantities sufficient to justify the hope that artificial radioactive substances may, in the near future, replace radium in medical work.

Exercises. — 1. What justification has been obtained in this chapter for the use of $O = 16$ rather than $H = 1$ as a basis for atomic weights?

2. Show clearly, following the method used for Cl on p. 478, the difference between the isotopic atoms of lithium (6 and 7); bromine (p. 477); and xenon (124, 126, 128, 129, 130, 131, 132, 134, 136).

3. What are the percentage compositions of $NaCl^{35}$ and $NaCl^{37}$?

4. How many varieties of chlorine molecules are present in gaseous chlorine?

5. Given the fact that isotopic atoms have the same volume, calculate the density of deuterium oxide D_2O in the liquid state at 4° and in the solid state at 0° (pp. 162–3).

6. What would be the density of the heaviest possible form of water, tritium oxide T_2O^{18}?

7. What physical properties, discussed in this book, could be utilized for the separation of chlorine into its two isotopes?

8. If there are two isotopes of chlorine, and eight of lead, how many varieties of lead chloride $PbCl_2$ are possible? In what respects would these varieties be different? In what respects would they be identical?

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CHAPTER XXVIII

ATOMIC STRUCTURE AND VALENCE

So far we have concentrated our attention on the nucleus of the atom. However, inasmuch as changes in the nucleus do not occur except in radioactive transformations and artificial transmutations, whereas in ordinary chemical reactions it is the exterior electrons that are affected, the *arrangement of these exterior electrons* with respect to the nucleus is an important point which we must not omit to consider. Two alternative theories have already been developed in this connection and a third is just getting under way. While these theories are in many points contradictory, yet each supplies us with certain ideas which are necessary to fill in the complete picture, and we may assume that ultimately some single generalization will be devised which will bring all of the three into perfect harmony. In view of its priority of development, we shall take up first what is known as the *octet theory.*

The Octet Theory. — The electrons surrounding the nucleus are arranged, according to this theory, developed mainly by Lewis and Langmuir, in successive concentric shells. The *total number of electrons in these shells* must be equal, since the atom as a whole is electrically neutral, to the *number of free protons in the nucleus,* in other words, to the *atomic number.*

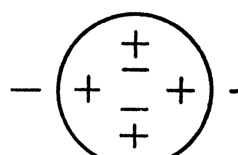


FIG. 137. Helium Atom (diagrammatic only).

The case of the **hydrogen** atom (atomic number = 1) has already been considered (p. 472). The **helium** atom (atomic number = 2) has two electrons, which are supposed to be situated on opposite sides of the nucleus (Fig. 137) — a very stable arrangement.

No more electrons (it is assumed) can be contained in the first shell, hence in succeeding elements the additional electrons begin to build up a *second* outer shell. Only the electrons in this outer shell can be added to or lost in interactions with other atoms (see p. 69),

and it is found that, for all of the next 8 elements from **lithium** to **neon,** the tendency is either to lose electrons until none is left, or to gain electrons until a stable ring of 8 is formed. The arrangement of the electrons in this second shell has been pictured * by Lewis as shown in Fig. 138. The electrons are assumed to occupy, as mean positions, the corners of an imaginary cube, in the center of which is the atomic nucleus. (To avoid confusing the diagrams, the nucleus and the inner shell of two electrons have been omitted.)

The valence of any one of these elements is therefore represented either by the number of electrons that can be lost (**positive valence**) or by the number required to complete a stable ring of 8

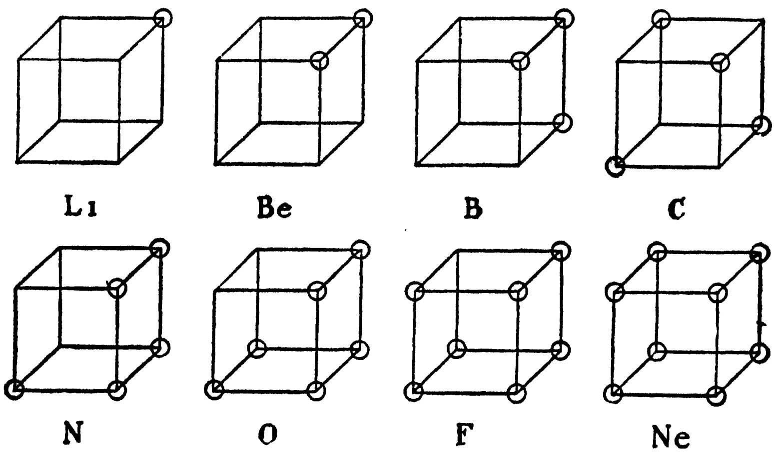


FIG. 138. Octet Theory—Lithium to Neon.

(**negative valence**). The next eight elements (sodium to argon) exhibit the same behavior. The electron arrangements for the succeeding elements in the Mendelejeff periodic system, when we leave the short series of 8 and arrive at the long series of 18, become rather less obvious, and the question of variable valenoy is not so easily explained. We shall consequently postpone the consideration of the positions assumed by the exterior electrons in these heavier elements until a later section (pp. 498–9).

Meanwhile, it may be noted that the "octet theory" is, in some respects, an outgrowth and amplification of a much older conception of Abegg and Bod-

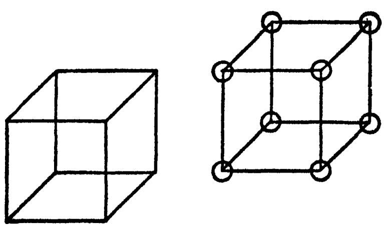
* The picture is now recognized to be merely a help to the imagination, but although it is quite imaginary its helpfulness remains (see p. 501).

länder. These two chemists noted in 1899 that many elements have different valences according as they are united with electropositive or electronegative elements. The usual valences of the metals are positive, and of the non-metals negative. These were called by Abegg and Bodländer the *normal valences*, and the valences of opposite polarity were called *counter-valences.* The sum of the maximum normal and counter-valences, as seen in the following table, is a constant and equal to 8.

The germ of the same idea will also be noted in the discussion on periodicity of valence in the Mendelejeff system (p. 443).

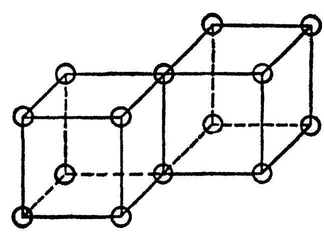
Element	Compound	Normal Valence	Compound	Counter-valence	Sum of Valences
Chlorine	HCl	1	Cl_2O_7	7	8
Sulphur	H_2S	2	SO_3	6	8
Phosphorus	PH_3	3	P_2O_5	5	8
Carbon	CH_4	4	CCl_4	4	8

Co-Valence. — When combination takes place between two atoms (*e.g.*, Li and F) by loss and gain of electrons, we are left with a *polar compound,* such as **LiF** (Fig. 139), in which the con-



Li+ F−

FIG. 139. Typical Polar Combination.



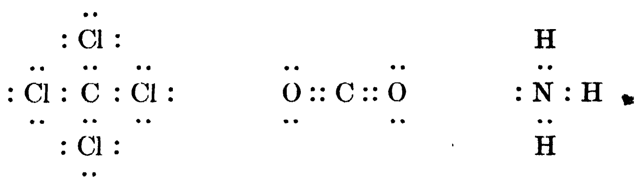
F_2

FIG. 140. Typical Non-polar Combination.

stituent ions are *essentially separate,* being held together only by the attraction of their opposite charges. An atom may also complete its stable ring of eight, however, by *sharing electrons* with another atom, as in the case of the **fluorine** molecule F_2 (Fig. 140). Similarly in **carbon tetrachloride** CCl_4, we may assume that all five atoms have completed their "octets," each chlorine atom holding a pair of electrons in common with the central carbon atom.

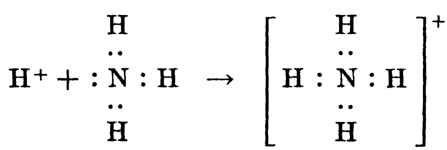
The number of pairs of electrons which an atom of an element can thus share with other atoms is called its **co-valence** (compare p. 149). The structural formulæ for some typical *non-polar compounds* on this basis are depicted below, each outermost electron

being represented by a dot, and each pair of dots between two atoms constituting a single co-valent bond.

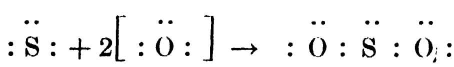


Carbon tetrachloride Carbon dioxide Ammonia

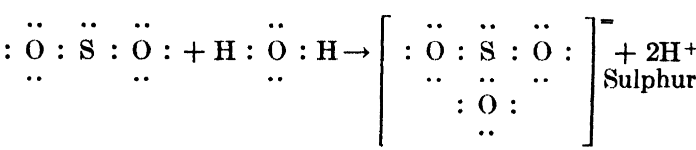
Semi-polar or Co-ordinate Valence. — It will be noted, when the above graphic formulæ are examined, that each atom concerned in a co-valent linkage has contributed one electron towards the shared pair. Combinations may occur, however, in which one atom contributes *both* electrons. Ammonia, for example, has a "lone pair" of electrons which it can donate in this manner, and the formation of ammonium-ion may be pictured thus:



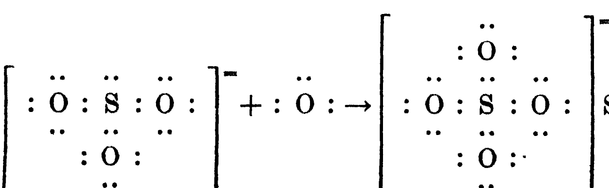
This type of union utilizes what is known as semi-polar, or co-ordinate, valence. The instances which follow are very instructive, and should be analyzed carefully by the student.



Sulphur dioxide



Sulphurous Acid



Sulphate ion.

The concept of co-ordinate valence is of particular value in elucidating the structure of the complex compounds of many metals, such as chromium and cobalt (see p. 880). The case of hydrogen merits immediate consideration.

To explain the physical and chemical properties of compounds such as water $(H_2O)_n$ (see p. 204) and potassium-hydrogen fluoride KHF_2, it is necessary to postulate that *hydrogen may possess a co-ordinate valence of two.* It is not considered tenable that the hydrogen atom should be associated with four shared electrons, however, two being its absolute maximum. Evidence has been obtained that the hydrogen atom in such compounds is in *resonance*, being attached first to one neighbor and then to another, the time of alternation being of the order of 10^{-15} second. Thus we may regard hydrogen in the ion HF_2^- as oscillating between the two fluorine atoms:

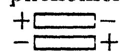
```
  ..      ..      ..      ..
: F :  H : F : ⇄ : F : H  : F :
  ..      ..      ..      ..
```

Care must be taken, in interpreting the electronic formulæ of compounds in which co-ordinate linkages occur, not to be misled with regard to the total valence of the atoms involved. Thus, from a casual comparison of the formulæ for CO_2 and SO_2 in the preceding paragraphs, the incautious student might assume that since the valences of carbon and of oxygen in the former compound are 4 and 2 respectively, the valences of sulphur and of oxygen in the latter must be only one-half of these values, namely, 2 and 1. Actually, of course, sulphur in SO_2 has donated just as many electrons towards the linkage with each oxygen atom as has the carbon in CO_2, so that total valences in the two compounds are essentially identical.

Similarly, the valence of nitrogen in ammonium-ion is **not** 4, as the beginner is apt to believe. The central nitrogen atom has donated one electron towards the union with each of three hydrogen atoms, but two electrons towards the union with the fourth hydrogen, so that its total valence is 5.

Atomic Structure and Chemical Affinity. — In cases where combination between two elements produces a compound (*e.g.* LiF) in which the arrangement of electrons is much more stable than in the original substances, we shall clearly obtain a considerable diminution in the internal energy of the system (see pp. 263–4) as the result of the interaction. **Chemical activity or affinity hence appears to depend, finally, upon atomic structure.** Where the electron arrangement is extremely stable, as with the helium family, the element will be *inert.* Where electrons are readily gained or lost,

as with the halogens or the alkali metals, the element will be *active,* and will form very stable compounds with such elements as assist most readily in the interchange.

Another important point to note is that in many molecules, even when no complete electron transfer (as in LiF, Fig. 139, p. 489) has taken place, we can distinguish positively and negatively charged portions. Thus, in SO_2, the fact that the sulphur atom has contributed both electrons towards the linkage with each oxygen atom makes it positively charged, while the oxygen atoms are negatively charged, although there is no actual ionic cleavage. For this reason, a co-ordinate linkage is frequently called a **semi-polar bond.** In the water molecule H_2O, similarly, although complete disruption into H^+ and OH^- very rarely occurs (see p. 318), we have a relatively-positive hydrogen atom and a relatively-negative hydroxyl group. When two such molecules approach one another, the positive part of one will obviously attract the negative part of another, and *vice versa.* In extreme cases, where the attractive forces are very strong, we consequently have the phenomenon of **dipole association,** which may be pictured thus: . But even where definite associated molecules are not formed, attractive forces may suffice to render the behavior of the molecules significantly different from what we should expect if they possessed no tendency at all toward cohesion (see p. 123).

We shall now proceed to discuss the later elements in the periodic system and the correlation of their electron arrangements with valence. For this purpose we shall return first to the Mendelejeff classification (p. 446).

A New Periodic System of the Elements.—The periodic system of Mendelejeff is not perfect, and its most obvious defects have already been enumerated (pp. 449–50). Are we prepared to take the next step to some broader generalization, which will amplify Mendelejeff just as he amplified Newlands? Thanks to recent work on atomic structure, we believe that we are.

If we examine Mendelejeff's table, we note that it has extended the range of applicability of Newlands' law of octaves by lengthening the third and fourth series from *seven* to *seventeen* (or, including the inert gases subsequently discovered, from *eight* to *eighteen*) elements. But still there remains a point of difficulty at either end of the system. Hydrogen is left out of the tabulation altogether. The elements of the rare earths make the fifth series unduly con-

gested, and we either have to arrange them in a helix or loop or leave them out too.

Suppose now we attempt to tabulate the elements in a different way, not trying to force them into series of fixed lengths, but simply writing them down in successive columns, taking them in the order of their atomic numbers, leaving blanks for elements still to be discovered and concluding each column with an inert gas. We obtain in this way the table shown in Fig. 141. Let us count up the number of elements in each column. The first column contains 2; the second 8; the third also 8; the fourth 18; the fifth again 18; the sixth 32; the seventh is obviously incomplete.

Now we can express these numbers in a regular mathematical series:

$$2 \times 1^2; 2 \times 2^2; 2 \times 2^2; 2 \times 3^2; 2 \times 3^2; 2 \times 4^2.$$

This series is far too striking to be due to chance. Evidently, then, **the inert gases occur at regular sequences in the list of elements.** Their numbers in the list (p. 475) are expressed by the ascending series:

$$2(1^2 + 2^2 + 2^2 + 3^2 + 3^2 + 4^2 + \ldots\ldots).$$

How about the other elements? Can we connect them up at all? Let us try to do so by drawing lines between those exhibiting similar properties. If an element resembles two others, let us draw lines to them both.

If we examine Fig. 141, now, we see that it fits the facts a great deal better than the Mendelejeff tabulation. *There must be some fundamental principle underlying it.* What that principle is, we are now in a position to elucidate.

The Bohr Theory.—According to this second theory of atomic structure, developed mainly by Bohr, the arrangement of the exterior electrons is not on a static "cubical" basis, but consists of a series of orbits around the nucleus. These orbits become more and more complex, the greater the number of electrons, and we have not space here to go into all the details of the Bohr theory, fascinating and comprehensive though they are. It will suffice at this point to state that the orbits may be divided into classes, which we may call "orbits of principal quantum number 1," "orbits of principle quantum number 2," and so on. These successive classes cor-

respond, in a way, with the concentric shells of the octet theory, although the ratio of the major axis to the minor axis in the orbits of different electrons of the same principal quantum number is not always the same. This fact is illustrated in Fig. 142, which shows the various types of orbits within each class. Each orbit may be

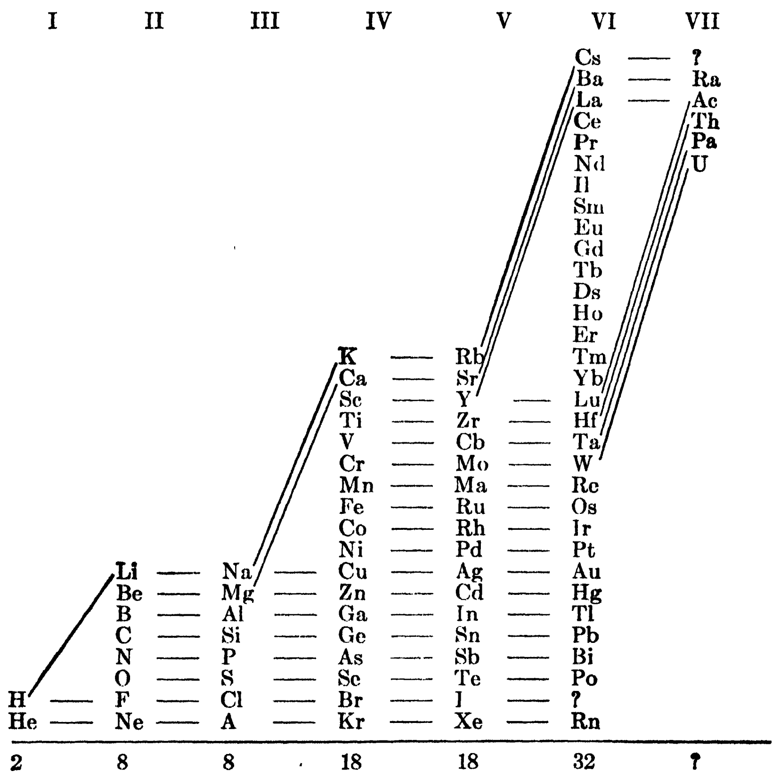


FIG. 141. Periodic Classification of the Elements (modified from Thomsen).

distinguished by assigning to it, besides a principal quantum number n, a subordinate quantum number n'. Thus we may speak of a 4_4 orbit (the largest circle in Fig. 142), a 2_1 orbit (the smallest ellipse in the same figure), and so on. Representations of the hydrogen atom (Fig. 143), the helium atom (Fig. 144), the lithium atom (Fig. 145), the neon atom (Fig. 146) and the sodium atom (Fig. 147), according to the Bohr theory, are here given, and should be

carefully analyzed by the student in connection with the accompanying text.

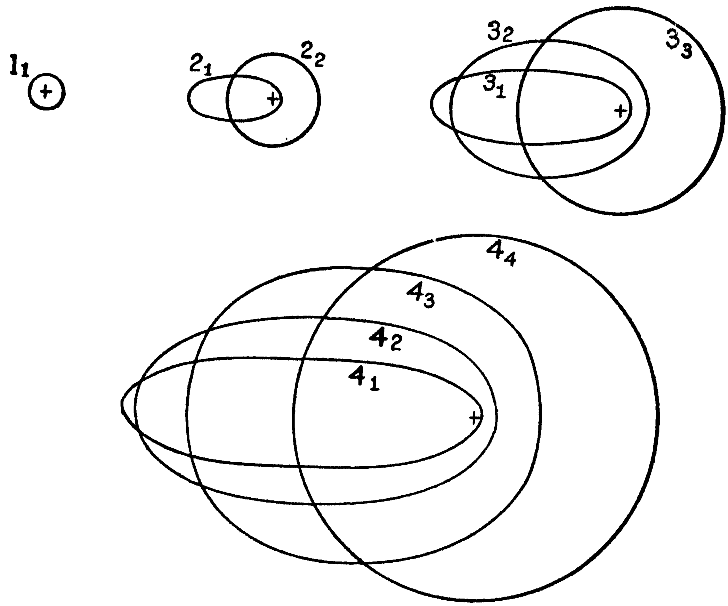


FIG. 142. Electron Orbits according to Bohr Theory.

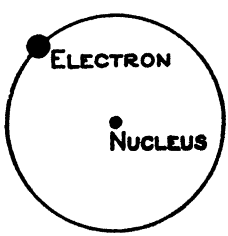


FIG. 143. Hydrogen. (Atomic No. 1.)

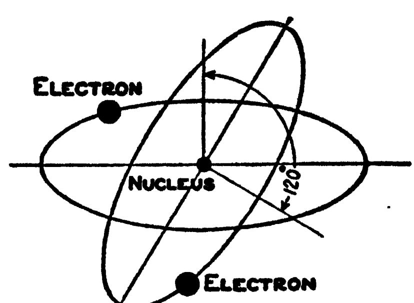


FIG. 144. Helium. (Atomic No. 2.)

Two points, however, may be mentioned here. First of all, as will be seen in Figs. 145–7, the orbits of all outer electrons are *pre-*

cessing ellipses (that is, the plane of the orbit rotates in space), owing to the perturbing effect of the two inner electrons. Secondly, the compactness of the neon atom as contrasted with that of sodium suggests immediately a reason for the inert character of the former element, and for the ease with which the latter rids itself of its widely-roaming outermost electron to become positively-charged sodium-ion.

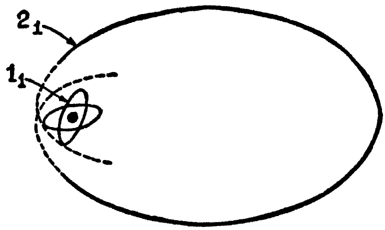


FIG. 145. Lithium. (Atomic No. 3.)

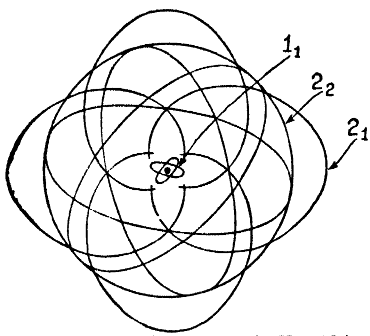


FIG. 146. Neon. (Atomic No. 10.)

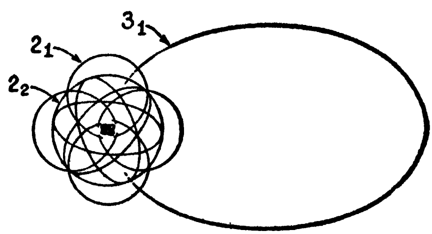


FIG. 147. Sodium. (Atomic No. 11.)

Arrangement of Electron Orbits. — Some rules regarding the arrangement of the electrons in their orbits may now be developed. The *maximum* number of electrons in each class is limited as follows:

First class; or orbits of principal quantum number 1	2 electrons
Second class; or orbits of principal quantum number 2	8 electrons
Third class; or orbits of principal quantum number 3	18 electrons
Fourth class; or orbits of principal quantum number 4	32 electrons

Note that these numbers follow the mathematical series: 2×1^2; 2×2^2; 2×3^2; 2×4^2. Before we proceed further, let us mention that it is immaterial to us, at this stage, whether the Lewis-Langmuir conception of electron shells or the Bohr conception of electron orbits is finally accepted. The former has been developed mainly from the chemical side, the latter mainly from the physical side. It is certain that the two ideas will ultimately be correlated to the satisfaction of all concerned, so that we can avail ourselves

of the best in both without question. The Bohr theory at present gives us a much more logical explanation of the whole periodic system of the elements, and is fundamentally on firmer ground than the Lewis-Langmuir theory, but it has not yet been extended with the same degree of success from atoms to molecules.

The first rule, then, in the Bohr theory is that the maximum number of electrons of quantum number n is given by the expression $2n^2$. To this first rule we must immediately add a second, which reads as follows: *The outermost class of orbits cannot, however, contain more than 8 electrons. The next to the outermost, similarly, cannot contain more than 18.*

This rule limits the electron arrangements to the following periods:

Number of Period	*Last Element in Period*	*Atomic No. of Last Element*	*Number of Electrons in Successive Classes* I	II	III	IV	V	VI
1	He	2	2	..	..	..	..	..
2	Ne	10	2	8	..	..	..	..
3	A	18	2	8	8	..	..	..
4	Kr	36	2	8	18	8	..	..
5	Xe	54	2	8	18	18	8	..
6	Rn	86	2	8	18	32	18	8

If we turn back now to Fig. 141 (p. 494), we shall begin to see the basis of our new periodic system, replacing Mendelejeff's.

The first period of elements is limited to two — hydrogen and helium. Hydrogen tends to lose its lone electron, becoming hydrogen-ion, or to fill up its first class by gaining one, becoming hydride-ion (p. 450). It is thus a member both of the alkali metal family and of the halogen family. Helium is inert; its first class is complete and it has no desire to start to form a second. The behavior of the elements from lithium to argon is exactly as was discussed under the octet theory, each element tending to dispose of its outermost class of electrons entirely or to complete the quota of this class to the maximum.*

After argon, however, there follow two periods of 18 elements, instead of 8, the introduction of the long period into Mendelejeff's

* Elements exercising positive valence frequently choose to keep *two* of their outermost electrons rather than to strip their shell completely. They thereby bring their atoms to an external imitation of the helium structure, rather than to a copy of the inert gas nearest to them. Thus tin and lead, whose atoms have four electrons in their outermost shell, may form with chlorine the compounds $SnCl_2$ and $PbCl_2$ as well as the compounds $SnCl_4$ and $PbCl_4$. This behavior is, indeed, very common among the heavier elements.

system thus being, for the first time, given a simple explanation. Furthermore, these two periods of 18 elements are followed by a period of 32, which includes perfectly (since $32 = 18 + 14$) the 14 rare earth elements for which no accommodation could be found by Mendelejeff.

Variable Valence. — In connection with these last three periods we must formulate a final rule. During the change of an inner class of orbits *from a stable group of 8 to one of 18, or from 18 to 32, there occurs a transition series of elements which can have more than one structure* (Bury). This rule accounts for the **variable valence** which we find in elements such as chromium, manganese, iron, copper, etc., as we shall now see.

Let us start from argon, the last element of the third period. Its electron arrangement is 2,8,8. The next element, potassium, is a typical alkali metal; its electron arrangement must be 2,8,8,1. Calcium, similarly, gives 2,8,8,2. But, as we proceed further, we find a more and more pronounced tendency for one or more added electrons to slip into the third set of orbits and start to fill it up towards its maximum of 18. *Thus we arrive at different electron arrangements for the same element. Some familiar examples are given below.*

Chromium	2,8,8,6 (chromates); 2,8,11,3 (chromic salts); 2,8,12,2 (chromous salts).
Manganese	2,8,8,7 (permanganates); 2,8,9,6 (manganates); 2,8,11,4 (manganites); 2,8,12,3 (manganic salts); 2,8,13,2 (manganous salts).
Iron	2,8,10,6 (ferrates); 2,8,13,3 (ferric salts); 2,8,14,2 (ferrous salts).
Copper	2,8,17,2 (cupric salts); 2,8,18,1 (cuprous salts).

This rule clarifies a great many chemical relationships. Chromates, manganates, and ferrates are derived from metals with shells of 2,8,8,6; 2,8,9,6; and 2,8,10,6 electrons respectively. They all have the same outer number of electrons, and we meet with similar arrangements in sulphur (2,8,6) and selenium (2,8,18,6). Hence chromates, manganates, and ferrates show close resemblances with each other, and also with sulphates and selenates. Note that *it is always the number of electrons in the outermost set of orbits that is of primary importance.* These are the **valence electrons.**

The same method of analysis may be applied to other elements, such as cobalt, nickel, palladium, the rare earth elements, platinum, gold and mercury. It is particularly worthy of note (see the follow-

ing table) how beautifully the rare earth elements fit into the new periodic system, and how the predominance of trivalency and the extreme similarity of chemical properties throughout the whole series are explained.

Element	Atomic Number	Electron Arrangement					
Lanthanum....	57	2,	8,	18,	18,	8,	3
Cerium........	58	2,	8,	18,	18,	8,	4 (ceric)
		2,	8,	18,	19,	8,	3 (cerous)
Praseodymium.	59	2,	8,	18,	20,	8,	3
Neodymium..	60	2,	8,	18,	21,	8,	3
Illinium.......	61	2,	8,	18,	22,	8,	3
Samarium.....	62	2,	8,	18,	23,	8,	3
Europium.....	63	2,	8,	18,	24,	8,	3
Gadolinium....	64	2,	8,	18,	25,	8,	3
Terbium.......	65	2,	8,	18,	26,	8,	3
Dysprosium...	66	2,	8,	18,	27,	8,	3
Holmium......	67	2,	8,	18,	28,	8,	3
Erbium........	68	2,	8,	18,	29,	8,	3
Thulium.......	69	2,	8,	18,	30,	8,	3
Ytterbium.....	70	2,	8,	18,	31,	8,	3
Lutecium......	71	2,	8,	18,	32,	8,	3
Hafnium......	72	2,	8,	18,	32,	8,	4

It will be evident, also, from the above table that hafnium, with atomic number 72, cannot possibly fall into the rare earth family, but functions instead as a quadrivalent element, resembling zirconium (2, 8, 18, 8, 4).

It is of importance, finally, to mention that the elements which possess incomplete inner shells with labile electrons are precisely those same elements which give **colored ions.** Rare earth elements such as praseodymium and neodymium, as well as chromium, manganese and copper, are all in this class.

The transfer of an electron from one orbit to another involves the absorption or evolution of a definite amount of energy, called a *quantum,* or of an integral multiple of this amount. The German physicist Planck put forward in 1900 the hypothesis that, just as matter was not continuous but made up of definite minute particles or atoms, so energy also was not continuous but existed only in definite indivisible units or quanta. The application of Planck's **quantum theory** has been just as fruitful in its results during this century as was the application of Dalton's atomic theory a century earlier. For example, Bohr has calculated, using classical dynamics, what wave-lengths the energy emitted or absorbed in typical orbital changes for atoms of different elements should possess, and has found that the calculated

values are *in exact agreement* with the lines on the spectrum of the element in each case.

The Atom and Wave Mechanics. — The beauty of the Bohr theory of the atom is so evident that a bitter feeling of disappointment is arising in many quarters as the conviction is gradually forced upon us that, after all, its foundations are not firmly fixed. A negative electron revolving around a positively charged nucleus should, accordng to classical dynamics, radiate energy. But if atoms really did radiate out energy in this way, the exterior electrons would fall slowly but surely into smaller orbits and finally drop into the nucleus. We know that this does not happen, since the atom is a stable affair and does not collapse with time.

In 1925 a French physicist, Louis de Broglie, attempted to apply the new mathematical ideas developed by Einstein to the Bohr type of electron. De Broglie found that, in order to get his equations to fit, it was necessary to assume that an electron revolving in its orbit around the nucleus was attended by a group of waves. We do not need to worry ourselves as to what the waves consist of; as a matter of fact, we do not know yet what light-waves consist of — they are merely, as Lord Kelvin said, "the nominative of the verb to undulate." These waves are born a little behind the electron and die out a little way ahead. But the electron moves so fast, and its orbit is so small, that the possibility had to be considered that the wave series might persist all around the orbit. If this should be the case, then the orbit would have to be such that the waves would not annihilate one another; crest must meet crest, and trough meet trough. When the necessary calculations were made with this point in mind, de Broglie found that the only possible orbits meeting such conditions were the orbits already postulated by Bohr.

This was all very promising and seemed so far to strengthen the Bohr theory, but now an Austrian physicist, Schrödinger, entered the field and said, "If the waves work so well, why a material electron at all?" Diving deep down into the waves with all the latest mathematical equipment, Schrödinger finally emerged with some involved equations in his grasp which show that the corpuscular electron is, indeed, unnecessary. In place of it we have the nucleus surrounded by a vibrating halo, an undulating aura, a pulsating nebula, or whatever else you like to call it. This is electrical in its nature, and the density of its charge fluctuates at different points, but the halo is brightest, the aura is most pronounced, or the

nebula is densest around the path of each little hard electron that, as such, isn't there any more. The nucleus degenerates into an electrical hole in the centre of the aura.

According to this latest theory of atomic structure, any pictorial representation of the atom (as given on pp. 488–9 and 495–6) is illusory. Nevertheless it is certain that chemists will continue to utilize atomic models in preference to intangible equations, and it is equally certain that valuable theoretical and practical results will continue to develop therefrom. An excellent example is given in the section immediately following.

Ortho- and Para-hydrogen. — In the hydrogen atom (Fig. 143), not only does the electron revolve around the nucleus, but the nucleus has a spin of its own. There are thus *two* kinds of molecular hydrogen possible, depending on whether the two nuclei are spinning in the same, or in opposite, directions. In accordance with this, it has been found that two kinds of molecular hydrogen do indeed exist, **ortho-hydrogen** and **para-hydrogen.** Ordinary hydrogen is a mixture of the two in the ratio of three to one. Orthohydrogen is slowly converted to para-hydrogen by pressure and cooling, and adsorption on charcoal (see p. 623) at liquid air temperature gives practically pure para-hydrogen. The physical properties of the two forms are very slightly different.

The Chemical Element. — In an earlier chapter (p. 25), we emphasized the fact that the results of recent research had entirely modified our original conception of the term **element.** The fundamental nature of the changes in our ideas will have become apparent to the student in the course of the last three chapters. Elements are **not** incapable of decomposition, for the fact that their atoms are all built up of the same protons and electrons shows that it is *possible* to transmute any element into any other, provided the proper procedure is followed to effect the necessary rearrangement.

It is certain, then, that atoms are not **indivisible.** Furthermore, the atoms of the same element are **not** all exactly similar to one another, nor are they equal in mass. There exist, for example, two species of lithium atom, one with an atomic mass of 6, the other with an atomic mass of 7. The nucleus of the former contains six protons and three electrons, the nucleus of the latter contains seven protons and four electrons. Each species of lithium atom, however, contains three *external* electrons, following similar orbits (Fig. 152),

and although certain physical properties (those dependent on mass) differ, *all* chemical properties (so far as we have experience of at present) are identical.

Not only do many atoms of the *same* element have *different* masses, but atoms of *different* elements may possess the *same* mass! Selenium, for example, with an atomic weight of 79.2, is found by the mass-spectograph to consist of a mixture of six isotopes, with atomic masses of 74, 76, 77, 78, 80 and 82, respectively. Krypton, with an atomic weight of 83.7, also consists of a mixture of six isotopes, with atomic masses of 78, 80, 82, 83, 84 and 86 respectively. The three heavier isotopes of selenium, therefore, are identical in mass with the three lighter isotopes of krypton. Atoms of different elements which possess the same mass are called **isobares.** Examples are very frequent among the radioactive elements, as may be seen from the table on page 468.

Although isobares have the same mass, they do **not** have the same chemical or physical properties; in fact, they differ absolutely in every respect *except* atomic mass. That this is the case is due to the fact that the arrangements of electrons in their nuclei and in their external orbits are essentially different. The **atomic number** of selenium is 34, and that of krypton is 36. To take a specific example, then, an atom of selenium with mass 78 contains 78 protons and 44 electrons in its nucleus, and its 34 external electrons fall into successive groups of 2,8,18,6; while an atom of krypton with the same mass contains 78 protons and 42 electrons in its nucleus, and its 36 external electrons fall into successive groups of 2,8,18,8. The outermost **valence electrons,** as we have seen, are those which essentially determine the chemical properties of the atom, and consequently *isobares* are quite diverse, while *isotopes* are identical.

The above illustrations suggest a tentative definition of the term element, in accordance with the demands of modern theory. An **elementary substance** may be defined as a substance which consists of atoms all possessing the same atomic number, or nuclear charge (p. 474). A **compound,** on the other hand, consists of atoms possessing different nuclear charges, in definite and simple numerical ratios.

Chemistry "within the atom" is still in its infancy, but it cannot be doubted that its development will lead to additional results of the greatest importance in the near future. The facts presented in this volume were almost all derived on a purely *experimental* basis, and the construction of hypotheses to correlate and explain these facts has been a long and painful process. On the

basis of atomic structure, however, the next generation of chemists will be able to *predict* physical and chemical properties in advance. A multitude of new facts will thus be brought to light, and many new applications of chemistry to industry will become evident.

Exercises. — 1. Picture the arrangement of the electrons in the elements from sodium to argon according to the Lewis-Langmuir theory (p. 488).

2. Discuss why water is so active in forming compounds with other substances, *e.g.*, oxides of non-metals, oxides of metals, salts (pp. 173, 490).

3. Draw diagrams showing the electron arrangements in the following molecules: hydrogen sulphide, oxygen (O_2), ozone (see p. 440), sulphuryl chloride (p. 434).

4. Why is phosphorus quinquivalent with respect to oxygen, but only trivalent with respect to hydrogen? Give the graphic formulæ for PH_3 and P_2O_5.

5. What various electron arrangements for cobalt (p. 910), nickel (p. 912), platinum (p. 818), gold (p. 813), mercury (p. 795), and thallium (p. 766) are indicated by their several series of compounds? Write each arrangement, following the models on p. 498.

6. Are the metals and the non-metals scattered indiscriminately about the table of the elements, as shown in Fig. 141, or can you draw a single straight line through the table, separating the two classes?

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CHAPTER XXIX

NITROGEN AND AMMONIA

It is time now to return to the atmosphere, of which the most plentiful component, nitrogen, has not yet been discussed.

History of Nitrogen. — Nitrogen was first recognized to be a distinct substance by Rutherford (1772), Professor of Botany in the University of Edinburgh, who named it mephitic air. Scheele showed that it was present in the atmosphere. Lavoisier recognized it to be an element, and named it *azote* (Greek, *without life*), because it did not support life. The English name records the fact that it is an important constituent of niter KNO_3.

The Chemical Relations of the Element Nitrogen. — In compounds with hydrogen and the metals nitrogen is trivalent, while in those containing oxygen and other negative elements it is frequently quinquivalent. It is a non-metal, for its oxides are acidic (p. 174). The organic compounds containing nitrogen are very numerous and possess highly characteristic properties. Some, like nitroglycerine and guncotton, are violently explosive; others, like antipyrine, show great physiological activity; still others, such as the aniline and other organic dyes, provide us with beautiful and useful coloring matters.

Occurrence. — Aside from the free nitrogen, which forms nearly four-fifths of the bulk of atmospheric air, much nitrogen is found in nature in combination. Potassium nitrate KNO_3 is formed in the soil by the action of bacteria upon animal matter, and sodium nitrate (Chile saltpeter) $NaNO_3$ is obtained from an immense deposit in Peru and Chile. Natural manures, such as guano, contain large quantities of nitrogen compounds, and owe their value as fertilizers to this fact. Nitrogen is an essential constituent of an important class of organic substances called *proteins,* which are found in plants, particularly in the fruit, and also in the muscles and other tissues of the animal body.

Preparation. — Nitrogen may be obtained from the air by simply removing the oxygen, *e.g.*, by allowing pieces of moist phosphorus (Fig. 148) slowly to oxidize in an enclosed specimen of air. This nitrogen is not absolutely pure, however, as it retains about one per cent of other gases — the "inert gases" of the atmosphere (p. 462). For commercial purposes, nitrogen is usually prepared by passing air over heated copper (p. 44) or by the fractional evaporation of liquid air (see p. 460).

Pure nitrogen can be obtained from pure compounds of nitrogen. Thus, ammonia gas may be passed over heated cupric oxide and the water vapor removed by bubbling the gas through sulphuric acid:

$$2NH_3 + 3CuO \rightarrow 3Cu + 3H_2O + N_2.$$

A *steady stream* of nitrogen is most easily made by heating sodium nitrite (p. 535) and ammonium chloride very gently along with a little water in a flask:

$$NH_4^+ + NO_2^- \rightarrow 2H_2O + N_2\uparrow.$$

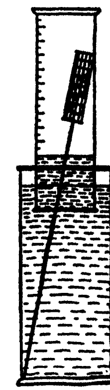


FIG. 148. Preparation of "Nitrogen" from Air.

Physical Properties. — Nitrogen is a *colorless, tasteless,* and *odorless* gas. Its *density* is indicated in the formula N_2 (mol. wt. $2 \times 14 = 28$). It is *very little soluble in water.* When liquefied it is found to boil at —196° and to freeze to a white solid at —210°.

Chemical Properties. — Nitrogen is chemically a rather indifferent gas. When passed through a tube over strongly heated lithium, calcium, magnesium, or boron, it forms definite chemical compounds, known as **nitrides,** in which it is trivalent. Thus, when magnesium is burned in the air, the white powder which is formed always contains some of the *nitride* of magnesium Mg_3N_2, along with much of the oxide MgO:

$$3Mg + N_2 \rightarrow Mg_3N_2.$$

The presence of the nitride may be shown by the odor of ammonia, given off when the ash is moistened with water:

$$Mg_3N_2 + 6H_2O \rightarrow 3Mg(OH)_2 + 2NH_3\uparrow.$$

The compounds with oxygen, such as nitric oxide NO and nitric acid HNO_3, and with hydrogen, such as ammonia NH_3, are of

immense commercial value, but, not being very stable, they are formed only in traces by direct union of the elements. The processes for utilizing these tendencies to union, feeble as they are, for manufacturing purposes, will be described under the compounds themselves.

The indifference of free nitrogen is doubtless due to the fact that its molecules N_2 are extremely stable (see p. 510). An **active form** of nitrogen, possibly N_3, discovered by Strutt, is produced by passing an electric discharge through the gas under low pressure. When the discharge is stopped, a yellow light is produced by the reversion of the nitrogen to the inactive form. A trace of oxygen seems to be required, possibly as a catalyst. With a little vapor of pentane C_5H_{12} in the tube, this active nitrogen gives hydrocyanic acid HCN (p. 574).

Ammonia

The interest in ammonia centers largely in the use of liquefied ammonia for refrigeration, in the employment of the gas in making carbonate of soda (see p. 715), and in the value of its compounds as fertilizers and explosives.

Manufacture. — Ammonia is formed when nitrogenous organic matter is heated, in absence of air. It was formerly made by distilling scraps of hoofs, horns, and hides. The solution of the gas thus obtained was called "spirit of hartshorn." The pungent odor of smoldering feathers, leather, or fur is, therefore, partly due to its presence in the escaping vapors. From the proteins of the original plants, **coal** derives a considerable proportion of nitrogenous matter. Hence, when coal is distilled for the making of coal gas, or, on a far larger scale, for the making of coke, much ammonia can be separated, by washing with water, from the mixture of gases produced. The aqueous solution is separated from the tar, neutralized with sulphuric acid, and evaporated to give the salt, ammonium sulphate $(NH_4)_2SO_4$.

The distillation of coal was formerly the chief source of commercial ammonia. In the United States, prior to the war, nearly all the coke was made in "beehive" ovens (see p. 625), in which the vapors issuing from the coal are burned, uselessly, on the spot. Since the war, these beehives have practically all been abandoned in favor of "by-product" ovens, in which the ammonia and innumerable other by-products are collected and utilized. In Scotland, oil-bearing shale is distilled for the purpose of extracting the petroleum, and much ammonia, liberated at the same time, is collected.

Synthetic Ammonia. — The most important method of manufacturing ammonia nowadays is by the direct union of hydrogen and nitrogen.

Exactly the same difficulties are encountered in the commercial operation of this reaction **(Haber's process)** as in the manufacture of sulphur trioxide by the contact process (p. 420), but in a greatly accentuated form. The union of the gases, although exothermic, is exceedingly slow in the absence of a suitable catalyst:

$$N_2 + 3H_2 \rightarrow 2NH_3 + 24{,}000 \text{ calories.}$$

In the presence of a *contact agent* — such as a finely-divided mixture of iron and molybdenum — combination is greatly hastened. Traces of other gases, however, such as carbon monoxide or hydrogen sulphide, must be very carefully eliminated from the reacting mixture, since they act as *poisons* on the catalyst, that is, they destroy or impair its activity.

The reaction is reversible, and much more incomplete than is the union of sulphur dioxide and oxygen under similar conditions. Since the forward action evolves heat, the reverse action is favored by raising the temperature (Van't Hoff's law, p. 284), hence the yield of ammonia in the equilibrium mixture becomes less and less the higher the temperature employed. Thus, under one atmosphere pressure, the proportions of the gases that combine in a mixture of one volume nitrogen and three volumes hydrogen are as follows: at 200°, 15.3 per cent; at 300°, 2.2 per cent; at 500°, 0.13 per cent; at 600°, 0.05 per cent; at 1000°, 0.004 per cent.

The preponderance of the reverse action, or in other words the tendency of ammonia to decompose into its constituent elements as the temperature is raised, makes it impossible to obtain high yields of ammonia by the Haber process at high temperatures, while at lower temperatures the combination is too tardy, even in the presence of a catalyst. Fortunately we are able to make use of another of our general laws, the principle of Le Chatelier (p. 285), to improve matters. It will be noted from the equation given above that the union of hydrogen and nitrogen to form ammonia is accompanied with diminution of volume, 1 volume of nitrogen + 3 volumes of hydrogen = 2 volumes of ammonia. Consequently *the forward action will be favored by increase of pressure.* In fact, under 200 atmopheres pressure the yield of ammonia in the equilibrium mixture is as follows: at 200°, 86 per cent; at 500°, 17.6 per cent; at 600°, 8.2 per cent; at 1000°, 0.9 per cent.

There still remains the question of speed of combination. This

decreases very rapidly as the temperature is lowered (compare p. 282), and no catalyst has yet been prepared which is sufficiently active to make the combination of nitrogen and hydrogen speedy enough to permit the process to be operated on an industrial scale

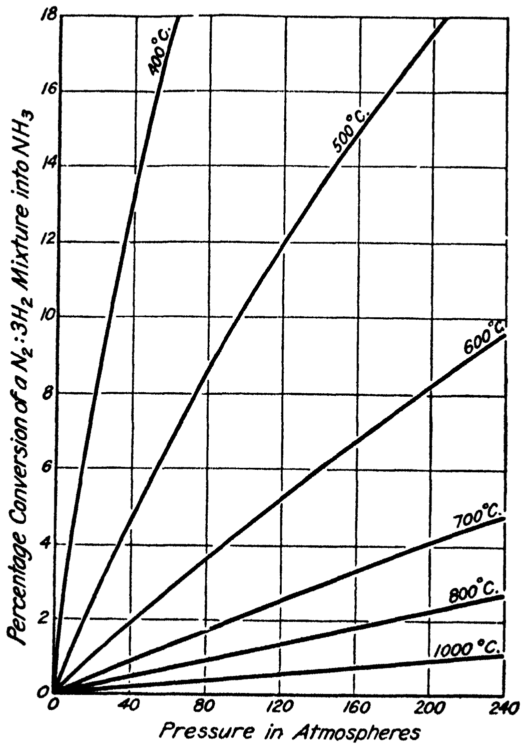


FIG. 149. Equilibrium Curves for Haber Process at a Series of Constant Temperatures.

much below 550°. A yield of about 14 per cent ammonia, therefore, is the best that can be obtained.

Details of the Haber Process. — The hydrogen may be obtained either as a by-product in an electrolytic process (p. 234), or by the action of steam on iron (p. 130), or by careful purification of water-gas (see p. 570). The preparation of pure hydrogen, it may be noted, is the most costly feature of the whole process. The nitrogen is usually obtained from liquid air (see also, however, p. 570). After removal of all impurities injurious to the catalyst, the mixed gases are passed under high pressure into the vessel

containing the catalyst. This consists of a steel "bomb" specially adapted to withstand the enormous pressure. After passing over the catalyst, the reaction mixture is cooled and its ammonia content removed either by refrigeration or by absorption in water. The residual nitrogen and hydrogen are returned to the plant for further treatment.

The ammonia obtained is used, in times of peace, mainly in the

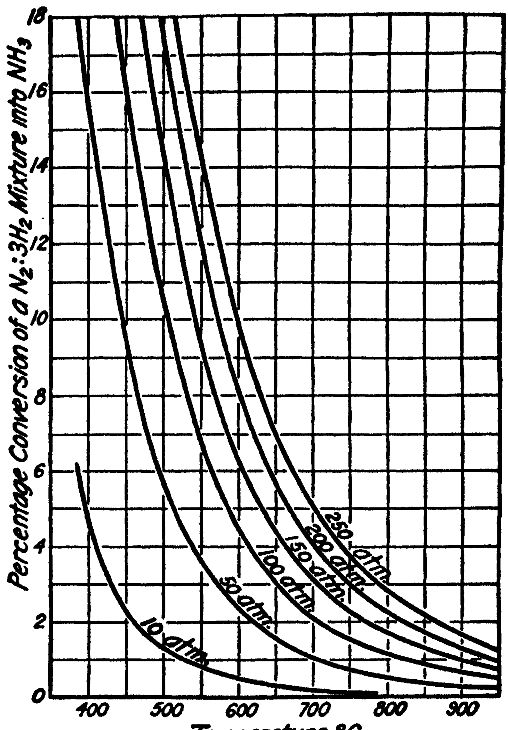


FIG. 150. Equilibrium Curves for Haber Process at a Series of Constant Pressures.

manufacture of *fertilizers,* such as ammonium sulphate. In war times, however, it is required more urgently for the production of *explosives.* Nitric acid HNO_3, which is necessary in the preparation of most explosives, is obtained from ammonia by oxidation (see p. 531). By the neutralization of nitric acid with ammonia, ammonium nitrate NH_4NO_3 is formed. A mixture of this substance with trinitrotoluene (p. 654) was used extensively as a high explosive during the Great War, under the name of **amatol.**

Synthetic ammonia may also be prepared by the calcium cyanamide process (see p. 734). But for these two processes, Germany would never have been able to continue fighting in the Great War beyond the first year. With all foreign supplies of nitrates (Chile saltpeter) cut off, the only other available source of ammonia was the by-product coke industry, and this was already being utilized almost to its maximum. In the allied countries, the Haber process during the war was not developed beyond the experimental stage.

The Haber process was first worked out in detail in 1904 by Haber and Le Rossignol. The catalysts first employed were very unsatisfactory, but an even more efficient catalyst than the Fe-Mo mixture mentioned on p. 507 (obtained by the reduction of a mixture of iron oxide, aluminium oxide, and potassium oxide) has recently been developed.

If the direct synthesis of ammonia could be carried out on a commercial scale under still higher pressures, say 1000 atmospheres, much higher yields would of course be obtained. The French **Claude process** is working in this direction, but it is doubtful whether the mechanical problems have, as yet, been successfully overcome.

Hydrogen, under a partial pressure of 150 atmospheres, leaks through a thick sheet of iron at 600° just about as easily as water does through a piece of filter-paper at 20°. The containers must therefore all be constructed of specially developed non-permeable steel alloys. In view of the dangers involved in an explosion, a large margin of safety must be allowed for in their design.

Atomic Hydrogen. — The sluggishness of the reaction $N_2 + 3H_2 \rightarrow 2NH_3$ in the absence of a catalyst is explained by the fact that the initial steps necessary to this reaction — the dissociation of molecular hydrogen and nitrogen into atomic hydrogen and nitrogen — are strongly *endothermic*. The thermochemical equations are:

$$H_2 \rightarrow 2H - 100{,}500 \text{ calories}$$
$$N_2 \rightarrow 2N - 210{,}000 \text{ calories.}$$

Although, therefore, the heat evolved in the final stage — the union of atomic hydrogen and nitrogen — is sufficient to make the total reaction *exothermic* (compare p. 264), this stage normally gets practically no chance to occur. In the presence of a suitable catalyst, however, the hydrogen and nitrogen are adsorbed (see p. 623) on the finely-divided surface of the catalyst in a quasi-atomic state, and the formation of ammonia is thereby considerably facilitated.

All endothermic reactions are favored by raising the temperature (p. 284), and consequently it is found that molecular hydrogen at an exceedingly high temperature is largely decomposed into atomic hydrogen H (see p. 190). When these single atoms recombine, an enormous amount of heat is liberated, and this fact has now been put to use in the hydrogen arc welding torch. In this torch a jet of hydrogen gas passes through an electric arc and is converted into atomic hydrogen. Immediately beyond the arc the atoms recombine, and the flame which they form in so doing is very much hotter even than that of the oxy-acetylene torch (p. 586), and may be employed very advantageously in making welds of particularly refractory metals.

Preparation of Ammonia in the Laboratory. — In the laboratory, ammonia is most readily made by heating a salt of ammonium, such as the chloride or sulphate, with slaked lime $Ca(OH)_2$:

$$Ca(OH)_2 + 2NH_4Cl \rightarrow CaCl_2 + 2NH_4OH.$$

The ammonium hydroxide, formed by the double decomposition, immediately decomposes: $NH_4OH \rightarrow NH_3 + H_2O$. To free the gas from water vapor, it is passed through a tower filled with quicklime (Fig. 151).

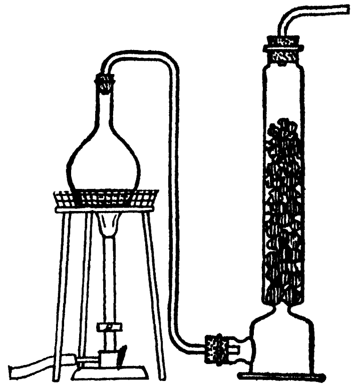


FIG. 151. Laboratory Preparation of Ammonia.

Sometimes, a stream of gas is generated by warming commercial ammonium hydroxide solution (*aqua ammonia*), and drying the gas as above. Liquefied ammonia is obtainable in small iron cylinders, and is a convenient source when much of the gas is required.

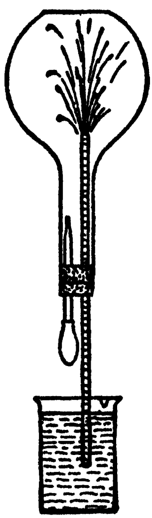


FIG. 152. Fountain Experiment.

Physical Properties. — Ammonia is a *colorless* gas. It has a soapy *taste*, and a very pungent *odor.* Its *density*, recorded in the formula NH_3, indicates that it is only about half as heavy as air. It is easily *liquefied*, boiling at —33.5°, and exerting a pressure of 6 atmospheres at 10°. The gas is exceedingly *soluble* in water (1 vol. water dissolves 1300 vol. of NH_3 at 0°).

The extreme solubility in water may be shown by the "fountain" experiment (Fig. 152). The flask is filled with ammonia by downward displacement of air. The long tube is closed by a short rubber tube and a clip at the bottom (not shown). The "dropper" contains water, and is closed at the tip with soft wax. A few drops of water, squirted into a flask by pinching the "dropper," dissolve at once so much of the gas that a partial vacuum is created and the water rushes in, like a fountain, through the longer tube, when the clip is opened. Under the best conditions the flask will be almost completely filled.

Liquefied ammonia is **used in refrigeration.** In evaporating at $-33.5°$ it absorbs 330 calories per gram. Water alone, among common liquids, has a greater heat of vaporization. To freeze one gram of water at 0°, 80 calories have to be removed. Thus 1 gram of liquid ammonia will convert more than 4 grams of water into ice.

Fig. 153 shows one arrangement diagrammatically. The ammonia gas, obtained from a cylinder of liquid ammonia, is driven by the pump *F* along the tube *E* and is liquefied in the tube coiled in the tank *AB*. Cold water circulating through *AB* removes the heat produced by the compression and liquefaction of the gas. The liquid ammonia is allowed to drip through the stopcock *G* into the lower coil and there it evaporates. In doing so, it takes heat from a 30 per cent solution of calcium chloride in water. This cooled brine leaves the tank at *D*, circulates through another tank, in which water-filled ice molds are suspended, and returns to *C*. When used for cooling storage-rooms for meat, the brine circulates through pipes in the same way. The machine is constructed of iron, because copper and brass are corroded by ammonia.

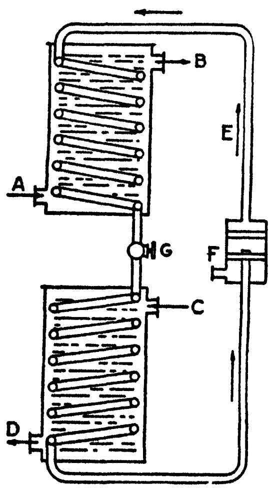


Fig. 153. Ammonia Refrigeration Apparatus.

Chemical Properties. — Ammonia, as we have seen, is not very **stable,** and decomposes rapidly and almost completely at 700°. A discharge of sparks from an induction coil has the same effect, so that a sample of the gas, confined over mercury in a eudiometer (Fig. 76, p. 159), may be shown to double in volume by continued sparking. Every two molecules give four:

$$2NH_3 \rightleftarrows 3H_2 + N_2.$$

Ammonia **reduces** many oxides, when the latter are heated and the gas is led over them:

$$3CuO + 2NH_3 \rightarrow 3Cu + 3H_2O + N_2.$$

A jet of ammonia may be ignited in pure oxygen (not in air) to give steam and nitrogen. By careful regulation of the oxidation temperature, nitric oxide NO may also be obtained (see p. 531).

Chlorine and bromine (vapor) combine with the hydrogen and liberate nitrogen:

$$2NH_3 + 3Cl_2 \rightarrow N_2 + 6HCl.$$

When **metals** capable of uniting with nitrogen (p. 505) are heated in a stream of ammonia gas, hydrogen is displaced. Magnesium gives magnesium nitride:

$$2NH_3 + 3Mg \rightarrow Mg_3N_2 + 3H_2.$$

Sodium and potassium, however, give amides (compounds containing the group NH_2), such as sodamide $NaNH_2$:

$$2NH_3 + 2Na \rightarrow 2NaNH_2 + H_2.$$

The most striking property of ammonia is that it **combines with acids,** giving ammonium salts. It **combines also with water** at low temperatures to give ammonium hydroxide NH_4OH and ammonium oxide $(NH_4)_2O$, white solids melting around $-80°$. These compounds are unstable at ordinary temperatures, so that a solution of ammonia, in a great excess of water, is the only form of ammonium hydroxide convenient for use.

Ammonium Hydroxide NH_4OH. — This substance, as indicated by the way in which we have written its formula, is a **base,** the compound positive radical NH_4 playing the part of a univalent metallic element, such as Na or K.

As a base, ammonium hydroxide, although rather weak (little ionized), turns red litmus blue, possesses the characteristic soapy taste and feeling, and enters into double decomposition with acids, neutralizing them:

$$NH_4OH + HCl \rightarrow H_2O + NH_4Cl.$$

The salts, obtained by evaporation, are, of course, identical with those formed by union of ammonia with the same acids.

Ammonium hydroxide used to be known as "volatile alkali," in reference to the fact that it decomposes into its constituents $(NH_3 + H_2O)$, both of which are volatile, while the other alkalies (NaOH, etc.) are not volatile, but "fixed." This property was utilized in the laboratory method of making ammonia (p. 511). Ammonium hydroxide solution is sold under the name of **household ammonia,** and is used, in washing and cleaning, to soften the water.

It may be remarked here that chemists now do not regard the weakness of NH_4OH as an electrolyte as due to any disinclination of NH_4OH to break up into NH_4^+ and OH^-. Under the theory of complete ionization, indeed, molecular NH_4OH is considered to be just as incapable of existence in aqueous solution as molecular NaOH or KOH. The low conductivity of ammonium hydroxide is ascribed instead to the tendency of NH_4^+ and OH^- to react and give NH_3 and H_2O (see p. 341). If the whole series of equilibria is written thus:

$$NH_3 \text{ (gas)} \rightleftarrows NH_3 \text{ (dissolved)} + H_2O \rightleftarrows NH_4^+ + OH^-$$

it will be seen that this point of view is entirely consistent with the experimental facts.

The Salts of Ammonium. — The salts are all strong electrolytes in aqueous solution, giving NH_4^+ as the positive ion:

$$(NH_4)_2SO_4 \rightarrow 2NH_4^+ + SO_4^=.$$

When *heated,* dry, in a tube, they are decomposed. Most of them give ammonia and the acid. When the latter is volatile, the whole material of the salt is thus converted into gas. The acid and the ammonia reunite to form the solid salt when the vapor reaches a cool part of the tube (sublimation, p. 350):

$$NH_4Cl \text{ (solid)} \rightleftarrows NH_4Cl \text{ (gas)} \rightleftarrows HCl + NH_3.\text{*}$$

This behavior distinguishes ammonium salts from those of the typical metals, for, with the exception of mercury salts, most other salts are not easily and completely volatilized. The use of ammonium chloride (sal ammoniac) in **soldering** depends on the dissociation of the salt, by the heat of the iron, and the action of the liberated hydrogen chloride on the oxide which covers the surface of the metal to be soldered.

Some ammonium salts, like the nitrite (p. 505) and nitrate (p. 537), when heated alone, give no ammonia. Conversely, substances containing proteins (*e.g.,* gelatin), when heated, do give ammonia. Hence, liberation of ammonia on simple heating is not decisive proof that a substance is a salt of ammonium.

* Just as perfectly dry NH_3 and perfectly dry HCl in the gaseous state do not combine (p. 229), so it has been found that perfectly dry ammonium chloride, when vaporized, shows no signs of dissociation, the vapor density being identical with that demanded by the formula NH_4Cl. For some other observations on the dissociation of the ammonium halides, see the account of the work of Alexander Smith in this field in the obituary notice at the beginning of this book.

The **test** for ammonium salts is to **warm** them, dry or in solution, **with a base,** when the *odor of ammonia* becomes noticeable:

$$\left.\begin{array}{l}(NH_4)_2SO_4 \rightarrow SO_4^{=} + 2NH_4^+ \\ 2KOH \rightarrow 2K^+ + 2OH^-\end{array}\right\} \rightleftarrows 2H_2O + 2NH_3\uparrow.$$

HYDRAZINE, HYDRAZOIC ACID, HYDROXYLAMINE

Hydrazine N_2H_4. — An aqueous solution of hydrazine hydrate N_2H_4,H_2O (more correctly, as will appear below, the *hydroxide* N_2H_5OH) may be obtained as follows. Nitric oxide NO and potassium sulphite K_2SO_3 combine to form a molecular compound (see pp. 524–6) with the formula $K_2SO_3,2NO$. This is reduced in water solution by means of sodium amalgam, a liquid alloy (see p. 695) of sodium and mercury, in which the former metal alone is active. The oxidation-reduction reactions involved are quite complex, and may therefore be written in detail according to the ion and electron method (p. 379):

$$SO_3^{=},2NO+6H_2O+6\ominus \rightarrow N_2H_5^+ + SO_4^{=} + 7OH^-$$
$$6Na \rightarrow 6Na^+ + 6\ominus$$

Adding: $SO_3^{=},2NO+6H_2O+6Na \rightarrow N_2H_5^+ + 6Na^+ + SO_4^{=} + 7OH^-$
In full: $K_2SO_3,2NO+6H_2O+6Na \rightarrow N_2H_5OH+6NaOH+K_2SO_4.$

The same substance is more easily made from certain organic derivatives. When the hydrate is distilled with barium oxide, under reduced pressure, hydrazine is liberated:

$$N_2H_4,H_2O + BaO \rightarrow N_2H_4\uparrow + Ba(OH)_2.$$

Hydrazine is a white solid, which fumes in moist air, giving the hydrate once more. It melts at 1.4° and boils at 113.5°. Hydrazine N_2H_4 bears the same relation to ammonia as hydrogen peroxide does to water, its structural formula (compare p. 368) being $H_2N — NH_2$.

Hydrazine hydrate freezes at about —40°, boils at 118.5°, and can be distilled without decomposition. Its aqueous solution is **alkaline,** showing that the substance exists therein, in part at least, as the hydroxide N_2H_5OH, and salts are formed by neutralization.

Hydrazoic Acid HN_3. — When nitrous oxide (p. 537) is led over sodamide at 200°, water is liberated and sodium hydrazoate remains behind:

$$NaNH_2 + N_2O \rightarrow NaN_3 + H_2O.$$

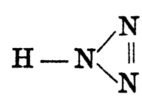
A dilute solution of the free acid is best obtained by distilling the lead salt with dilute sulphuric acid. A similar solution may be made more directly by adding cold nitrous acid (p. 535) to a cold aqueous solution of hydrazine hydrate:

$$N_2H_5OH + HNO_2 \rightarrow HN_3 + 3H_2O.$$

By repeated distillation of the solution the pure acid is obtainable. It boils at 37°. The operation is a dangerous one, as the pure acid is violently explosive, resolving itself into nitrogen and hydrogen with liberation of much heat. The acid has an odor resembling hydrochloric acid, and the sodium salt has a taste like sodium chloride. The silver salt is insoluble in water. Thus the univalent radical N_3 confers properties similar to the univalent radical Cl. The acid has a somewhat greater activity and degree of ionization than has acetic acid. Active metals, like magnesium, displace hydrogen from its solution. It neutralizes ammonium hydroxide and hydrazine hydrate, giving two salts, NH_4N_3 and $N_2H_5N_3$. Lead hydrazoate $Pb(N_3)_2$ is replacing mercuric fulminate (p. 800) in the manufacture of percussion caps.

Some doubt formerly existed as to the exact structural formula of hydrazoic acid. Two possible ways of representing it are as follows:

$$H - N = N \equiv N$$



Recent X-ray investigation on the crystal structure of azides has shown the first formula to be correct. Written electronically, it is

$$H : \ddot{N} :: N :: \ddot{N}$$

Hydroxylamine NH_3O. — This substance, like ammonia and hydrazine, unites with water to form a base, the formula for which may be written $NH_4O.OH$. On addition of a strong acid to this, salts are obtained, such as hydroxylamine hydrochloride NH_4OCl. This hydrochloride is one of the products formed when dilute nitric acid is reduced by means of tin and dilute hydrochloric acid. The oxidation-reduction reactions involved may again be developed by the ion and electron method:

$$NO_3^- + 8H^+ + 6\ominus \rightarrow NH_4O^+ + 2H_2O$$
$$3Sn \rightarrow 3Sn^{++} + 6\ominus$$

Adding: $NO_3^- + 8H^+ + 3Sn \rightarrow NH_4O^+ + 3Sn^{++} + 2H_2O.$

In full: $HNO_3 + 7HCl + 3Sn \rightarrow NH_4OCl + 3SnCl_2 + 2H_2O.$

By more complete reduction of part of the nitric acid, some ammonium chloride NH_4Cl is formed at the same time. To secure the salt of hydroxylamine, the tin ions are removed by means of hydrogen sulphide, which precipitates stannous sulphide. The filtered solution is then evaporated to dryness, the hydroxylamine hydrochloride is extracted from the residue with absolute alcohol, and this alcoholic solution is finally evaporated in turn. The hydrochloride is a white crystalline salt.

A better yield (80 per cent) is obtained by placing 50 per cent sulphuric acid (or 25 per cent HCl) in an electrolytic cell. The negative electrode is a pool of mercury, or a small piece of lead amalgamated with mercury, and nitric acid is allowed to flow very slowly from a tube on to the surface of the electrode. The cell is kept cool, and a high current density, by using a small mercury surface, is required for a good yield. The equation is substantially the same as that given above.

Anhydrous hydroxylamine is best obtained by heating the orthophosphate $(NH_4O)_3PO_4$ under reduced pressure:

$$(NH_4O)_3PO_4 \rightarrow H_3PO_4 + 3NH_3O \uparrow.$$

It is a white solid melting at 33° and boiling at 58° at 22 mm. pressure. Even before melting (above 15°), it begins to decompose, and explodes at or below 130°. In chemical behavior it is like ammonia. With water it forms a base which combines with acids, but is less active than ammonium hydroxide. It is a stronger reducing agent than ammonia, precipitating silver from a solution of silver nitrate.

The union with acids involves, as in the case of ammonia (p. 490), the utilization of a semi-polar or co-ordinate valence on the part of the nitrogen atom:

$$\begin{array}{c} \\ \mathrm{H} : \ddot{\underset{\cdot\cdot}{\mathrm{O}}} : \end{array}\begin{array}{c} \mathrm{H} \\ \ddot{\underset{\cdot\cdot}{\mathrm{N}}} \\ \end{array} : \mathrm{H} + \mathrm{H}^+ \rightarrow \left[\mathrm{H} : \ddot{\underset{\cdot\cdot}{\mathrm{O}}} : \begin{array}{c} \mathrm{H} \\ \ddot{\underset{\cdot\cdot}{\mathrm{N}}} \\ \mathrm{H} \end{array} : \mathrm{H} \right]^+$$

Halogen Compounds of Nitrogen. — When ammonium chloride solution is treated with excess of chlorine, drops of an oily liquid, **nitrogen trichloride,** are formed: $3Cl_2 + NH_4Cl \rightarrow NCl_3 + 4HCl$. It is extremely explosive, resolving itself into its constituents with liberation of much heat. The compounds $NHCl_2$ and NH_2Cl are also known.

When a solution of iodine in potassium iodide solution (p. 350) is added to aqueous ammonia, a brown precipitate is formed. This at ordinary temperatures has the composition NH_3,NI_3, and is commonly named **nitrogen iodide.** It may be handled while wet. When dry, if touched with a feather, it decomposes into its constituents with violent explosion.

Recently **nitrogen trifluoride** NF_3 has been obtained by the action of fluorine on ammonia. It is a colorless gas which, in contrast to the highly explosive NCl_3, is remarkably stable.

Exercises. — 1. Why can we not dry ammonia gas with concentrated sulphuric acid or with phosphorus pentoxide?

2. In view of the thermochemical equations on p. 510, can you suggest any reason why nitrogen, at ordinary temperatures, is such an inert element?

3. How could you separate a mixture of oxygen and ammonia?

4. Classify (p. 232), (*a*) the interaction of a nitride with water (p. 505), (*b*) the results of heating ammonium nitrite (p. 505) and (*c*) ammonium chloride (p. 514).

5. What weight of ammonia will be obtained by heating 10 g. of magnesium nitride with excess water? If this ammonia were dissolved in water, and the solution made up to 500 c.c., what would be the normality of the solution? To neutralize 25 c.c. of this solution, how many c.c. of 0.1 N hydrochloric acid would be required? How many c.c. of 0.1 N sulphuric acid?

6. What substances are present in ammonium hydroxide solution? When the liquid is heated, what happens to each? Formulate the system.

7. Re-state the thermochemical equation for the neutralization of ammonium hydroxide on p. 334 in terms of modern chemical theory.

8. Write the electronic formulæ of (*a*) ammonium hydrazoate, (*b*) hydrazine hydrazoate? What would you confidently expect to be the most striking chemical property of both these salts?

9. What are the ions of hydrazine hydrate? Formulate (p. 332) the neutralization of this base with sulphuric acid.

10. Why does not ammonia burn in air (p. 100)?

11. At 500° and 120 atmospheres total pressure, what is the percentage of the $N_2 : 3H_2$ mixture converted to ammonia when equilibrium is reached? What are the partial pressures of NH_3, N_2 and H_2 respectively in the equilibrium mixture? Use Fig. 149.

12. At 500° and 60 atmospheres total pressure, what is the percentage conversion in the same mixture? What are the partial pressures of NH_3, N_2 and H_2 respectively?

13. Show how Fig. 150 may be derived from Fig. 149.

14. Why do we dry ammonia gas with quicklime, not with calcium chloride (p. 722)?

15. What is the object attained by distilling under reduced pressure in making hydrazine and hydroxylamine (p. 367)?

16. Show that ammonium chloride furnishes an example of each of the three types of valence now recognized by chemists — electrovalence, co-valence and co-ordinate valence.

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CHAPTER XXX

OXIDES AND OXYGEN ACIDS OF NITROGEN

The names and formulæ of the oxides and oxygen acids of nitrogen are as follows:

Nitrous oxide N_2O	$\longleftarrow$	Hyponitrous acid $H_2N_2O_2$
Nitric oxide NO		
Nitrous anhydride N_2O_3	$\longleftrightarrow$	Nitrous acid HNO_2
Nitrogen tetroxide $N_2O_4 \rightleftarrows 2NO_2$		
Nitric anhydride N_2O_5	$\longleftrightarrow$	Nitric acid HNO_3
Nitrogen peroxide NO_3		

All the oxides are endothermal compounds (p. 260), yet, with the exception of the third and the last, they are all relatively stable. The acids, when deprived of the elements of water, yield the oxides opposite which they stand (p. 174). Conversely, excepting in the case of nitrous oxide, the anhydrides with water give the acids. All of these substances are made directly or indirectly from nitric acid — nitric anhydride by removal of water, the others by reduction. We turn, therefore, first, to nitric acid and its properties.

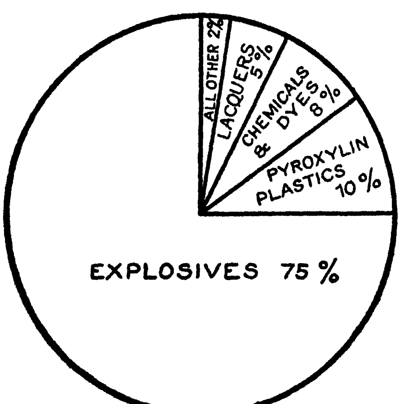


FIG. 154. Distribution of Nitric Acid in Industry.

NITRIC ACID HNO_3

Nitric acid HNO_3 is used in large quantities for making explosives like guncotton, picric acid and TNT, and plastics like celluloid, as well as innumerable drugs and dyes (see Fig. 154). Nitrates are largely used as fertilizers (p. 612).

Sources. — Sodium nitrate, or Chile saltpeter (*caliche*), is found in a desert region near the boundary of Chile and Peru, and chiefly in the former country. The deposit is about 5 feet thick, 2 miles wide, 220 miles in length, and contains 20 to 60 per cent of the salt. Purification is effected by recrystallization. Potassium nitrate, or Bengal saltpeter, is found in the soil in the neighborhood of cities in India, Persia, and other oriental countries. It arises from the oxidation of animal refuse (compare p. 614) through the mediation of nitrifying bacteria. The potash and lime in the soil, along with the product of oxidation of the nitrogen, give nitrates of potassium and calcium. The aqueous extract of this soil is treated with wood ashes, which contain potash K_2CO_3. It is poured off from the calcium carbonate thus precipitated, and is finally evaporated. The organic compounds of nitrogen originally contained in guano, a valuable fertilizer, are frequently found to have been changed into nitrates by nitrifying bacteria.

Manufacture. — Nitric acid is obtained in two ways, namely, by the action of sulphuric acid upon natural sodium nitrate (p. 423) and by oxidation of the nitrogen of the atmosphere. The processes which utilize the latter method will be referred to in a later section.

To obtain nitric acid from sodium nitrate, the salt is mixed with concentrated sulphuric acid in iron retorts and gently heated to drive off the nitric acid (compare p. 225). The sodium-hydrogen sulphate remains in the retort:

$$NaNO_3 + H_2SO_4 \rightleftarrows NaHSO_4 + HNO_3 \uparrow.$$

The vapor which comes over is condensed in glass tubes (cooled with water) and the acid collected in vessels of earthenware. Nitric acid boils at 86° (760 mm.), but, to prevent loss by decomposition (see p. 522), a lower boiling-point is secured by reducing the pressure in the whole apparatus.

In the laboratory the same action is employed, without, however, the reduction in the pressure.

The disposal of the residual sodium acid sulphate (technically known as **niter cake**) from the above process used to be a matter of some difficulty, and in view of its obvious economic importance a great deal of work has been done upon the problem in recent years. In the parallel process for the manufacture of hydrogen chloride, the temperature can be raised to the point where the acid sulphate reacts with a second batch of sodium chloride, giving the neutral sulphate (p. 225). This second stage can be only partially carried out here, however, because of the decomposition of nitric acid at higher temperatures. In order to avoid wasting the tremendous amounts of available

sulphuric acid remaining in niter cake, therefore, various uses for this material have gradually been developed, as illustrated in the accompanying diagram (Fig. 155).

Physical Properties. — Pure hydrogen nitrate (100% HNO_3) is a colorless, mobile liquid (sp. gr. 1.54), which freezes to a white solid (m.-p. —47°). It fumes strongly when its vapor issues into moist air (compare p. 224). An aqueous solution containing 68 per cent of the substance boils at 120.5°, while the pure acid, pure water, and all other mixtures, boil at lower temperatures. This 68 per cent nitric acid of constant boiling-point (p. 228) forms the "concentrated nitric acid" of commerce (sp. gr. 1.41).

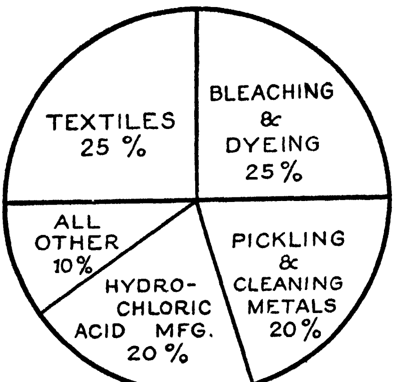


FIG. 155. Distribution of Niter Cake in Industry.

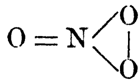
Chemical Properties. — Like chloric acid (p. 385), and other oxygen acids of the halogens, nitric acid is most stable when mixed with water. The pure (100 per cent) acid is slightly unstable at room temperatures, and it decomposes very noticeably while being distilled under atmospheric pressure at 86°:

$$4HNO_3 \rightarrow 4NO_2 + 2H_2O + O_2,$$

the distillate ("fuming" nitric acid) being colored brown by dissolved nitrogen tetroxide NO_2.

Nitric acid, when dissolved in water, is a typical **strong acid.** By interaction with hydroxides and oxides it forms **nitrates.** The nitrates of the metallic elements are all more or less easily soluble in water. When heated they decompose in one or other of three ways (see pp. 527, 535, 537). The individual nitrates, such as sodium nitrate and potassium nitrate, are described elsewhere.

When pure hydrogen nitrate is poured upon phosphoric anhydride, the latter combines with the elements of water, and distillation at a low temperature gives **nitric anhydride:** $2HNO_3 + P_2O_5 \rightarrow N_2O_5 \uparrow + 2HPO_3$. The anhydride is a white solid melting at 30°. It unites vigorously with water to form nitric acid. It decomposes spontaneously at 50° into nitrogen tetroxide and oxygen:

$2N_2O_5 \rightarrow 4NO_2 + O_2$. When ozonized oxygen is passed over nitric anhydride, a gas with a blue tint is produced, which contains the very unstable **nitrogen peroxide** NO_3. The structural formula of this compound is represented by .

Nitric acid is an **oxidizing agent** even when diluted with water. The multiplicity of the products into which it may be decomposed by reduction, however, renders separate treatment of this property necessary (see p. 532).

Nitric acid interacts energetically with many compounds of carbon to give **nitro-derivatives.** Many of these are of great importance as explosives. Their preparation and properties will be discussed in a later chapter (pp. 652–4).

Nitric acid produces substances of bright-yellow color, known as **xanthoproteic acids,** when it comes in contact with proteins, *e.g.*, in the skin, or in wool. Hence nitric acid stains woolen clothing yellow, and affects the skin in the same way. This reaction is used as a test for proteins.

Nitric Oxide and Nitrogen Tetroxide

Preparation of Nitric Oxide NO. — Pure nitric oxide is obtained by adding nitric acid to a boiling solution of ferrous sulphate in dilute sulphuric acid:

$$6FeSO_4 + 3H_2SO_4 + 2HNO_3 \rightarrow 3Fe_2(SO_4)_3 + 2NO + 4H_2O.$$

This action is used as a means of determining the quantity of nitric acid in a solution, or of nitrates in a mixture, by measurement of the volume of nitric oxide evolved.

Nitric oxide may also be obtained when sufficiently dilute nitric acid (sp. gr. 1.2) acts upon copper (see p. 532). This interaction furnishes the most convenient method of generating the gas in the laboratory. Direct union of nitrogen and oxygen to form NO can be effected only at very high temperatures (see p. 530).

Properties of Nitric Oxide. — Nitric oxide is a colorless gas. In solid form it melts at —164°, and the liquid boils at —152°. Its solubility in water is slight. The density of the gas shows the formula to be NO; and there is *no* tendency to form more complex molecules, such as N_2O_2, even at low temperatures.

This gas is the most stable of the oxides of nitrogen. Vigorously burning phosphorus continues to burn in the gas, nitrogen being set

free. Burning sulphur and an ignited taper, however, are extinguished.

Nitric oxide has two characteristic chemical properties. It unites directly with oxygen in the cold to form the reddish-brown nitrogen tetroxide:

$$2NO + O_2 \rightleftarrows 2NO_2.$$

The same result follows when it is led into warm concentrated nitric acid: $NO + 2HNO_3 \rightleftarrows 3NO_2 + H_2O$.

It also forms unstable compounds with a number of salts, the compound in the case of ferrous sulphate, $FeNO.SO_4$, being capable of existence in cold aqueous solution and possessing a brown color. The NO is part of the positive ion $FeNO^{++}$, and migrates with it (Manchot).

Since ferrous sulphate will first reduce nitric acid to nitric oxide (see above), and the excess of the salt will then give a brown color with the product, a delicate **test for nitric acid (or the NO_3^- ion)** is founded upon the above action. The substance supposed to contain a nitrate is mixed with a concentrated solution of ferrous sulphate, and concentrated sulphuric acid is poured down the side of the tube so as to lie below the lighter mixture (Fig. 156). At the surface of contact the sulphuric acid liberates the nitric acid, this is reduced to nitric oxide, the molecular compound is formed, and a brown layer is seen. Even when the amount of the nitrate is very small, the brown ring is distinctly visible, by contrast with the colorless liquids above and below it.



FIG. 156. Ring Test for Nitric Acid.

Molecular Compounds. — When substances formed by union of two compounds have a prevailing tendency to decompose into the same two materials, and exhibit the chemical properties of their constituents rather than individual ones of their own, they are often called **molecular compounds.** Thus the above substance $FeNO.SO_4$ gives off the nitric oxide again when warmed. Similarly hydrates (pp. 175, 689) are formed by union of salts or other substances with water, and are, for the most part, decomposed by solution. Double salts (p. 291), such as ferrous-ammonium sulphate $FeSO_4,(NH_4)_2SO_4,6H_2O$, of which very many are known, are of the same character. They are stable only in the solid form. There are also compounds of salts with ammonia (see pp. 722, 748),

and with carbon monoxide CO, one such compound being formed with cuprous chloride (p. 787).

The name *molecular compounds* is derived from the supposition that, in these compounds, the molecules of the components retain their individuality to some extent and are thus ready to be liberated. This is a crude attempt to explain the fact that the behavior is that of the constituents. It tries to differentiate molecular compounds from substances like calcium carbonate and phosphorus pentachloride. The former may be made by union of CaO and CO_2, but usually behaves rather as if composed of the radicals Ca^{++} and $CO_3^{=}$. The latter (p. 193) dissociates into PCl_3 and Cl_2, but with water gives phosphoric acid (compare p. 231), which is derivable from the pentachloride only. The distinction is of practical rather than theoretical importance, however, for there are all gradations in the behavior of molecular compounds. It is useful simply as a rough means of classifying and remembering certain facts.

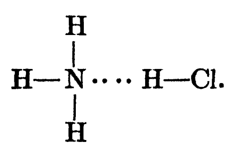
Distinguishing molecular compounds from ordinary compounds is further justified by the fact that the constituents of molecular compounds often seem to be saturated (p. 151), and no ordinary valences are available for holding the new material. Thus in $Ca^{II}Cl_2^{I}$ the ordinary valences are all saturated. Yet the salt forms the hydrate $CaCl_2,6H_2O$ with water $H_2^{I}O^{II}$, which is likewise a saturated compound. The conception of molecular compounds implies, therefore, the idea of a sort of *secondary valence*, or *valence of molecules*. Thus $FeSO_4$ forms $FeSO_4,7H_2O$ and $FeSO_4,(NH_4)_2SO_4,6H_2O$, and $FeSO_4,K_2SO_4,6H_2O$, in all of which *seven* other molecules are combined with it. The sulphates of other bivalent metals, such as zinc, nickel and magnesium, form molecular compounds of the same nature (see p. 691).

As noted already in the course of the above discussion, it is impossible to draw a sharp line between *molecular compounds* and compounds of the ordinary type. Any attempt to do so, whatever the basis employed to make the distinction, leads to pure arbitrary differentiations, which cannot stand strict analysis. Let us consider, for example, the three substances *copper sulphate pentahydrate, ammonium chloride,* and *calcium carbonate.* The first of these is almost invariably considered as a molecular compound in chemistry textbooks, the second is placed just about as frequently in one class as in the other, and the third is practically always regarded as a compound of the usual type. Yet examination shows all three substances to possess precisely similar characteristics. All three can be broken up into simpler compounds either by heating, or by reducing the partial pressure of their volatile constituents to a sufficiently low value. The dissociation equilibrium of calcium carbonate is, in point of fact, exactly analogous to that of hydrated copper sulphate, as will be shown in detail in later chapters (pp. 689, 724). Calcium oxide and carbon

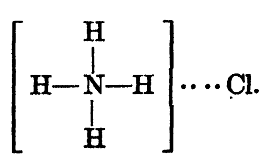
dioxide are saturated compounds, moreover, in just the same sense as are copper sulphate and water. It may be argued that the behavior of calcium carbonate in aqueous solution, where the ions Ca^{++} and $CO_3^{=}$ clearly exist, distinguishes it from blue vitriol, in the solution of which only Cu^{++} and $SO_4^{=}$ ions are postulated. There is very strong evidence, however (see p. 782), that the blue substance in the latter solution, which we usually call cupric-ion for simplicity, is really a hydrated cupric-ion $[Cu(H_2O)_x]^{++}$, and the acceptance of this fact immediately places copper sulphate pentahydrate in the same class as the other two compounds, in which the corresponding complex ions *may* be written $[H(NH_3)]^{+}$ and $[O(CO_2)]^{=}$.

This is another of the instances in chemistry where we find it convenient to classify substances or reactions into various groups, without being able to draw any definite boundaries between the groups. Thus polar compounds merge gradually into non-polar compounds (p. 149), metallic elements into non-metallic elements (p. 441), strong electrolytes into weak electrolytes (p. 299), and so on.

Werner's Co-ordination Theory. — Many chemists used to regard ammonium chloride as a compound in which the two simpler constituents are connected only by secondary (or auxiliary) valence. This auxiliary valence was represented by means of a dotted line, in contrast to the full line employed for primary valence, and the formula for ammonium chloride was accordingly written:



According to a theory first developed by Werner, there is a limit to the number of primary and secondary valences which an atom can employ. This limit Werner called the **co-ordination number;** it represents the *maximum number of atoms, radicals, or molecular groups (independent of their valences) that can be directly linked to a central atom.* In the case of the nitrogen atom, the co-ordination number is **four,** and since we are unable to distinguish any difference in behavior in any one of the four hydrogen atoms in NH_4Cl, Werner assumed that the affinity of the chlorine is equally distributed over the whole group, and consequently the formula is more properly written as follows:



If reference is made to the electronic formulæ on p. 490, it will be seen that the above representation of ammonium chloride has now been fully justified by the conception of **co-ordinate valence.** This type of valence was so named, indeed, because of its close connection with the co-ordination theory of Werner.

An exhaustive analysis of recent work by Sidgwick shows that the maximum co-ordination number for hydrogen is 2 (see p. 491), for the elements from lithium to fluorine it is 4, for the elements from sodium to bromine it is 6, and from rubidium onwards it is 8, with a possibility of 10 for elements nearer uranium. The reconciliation of co-ordination numbers greater than 4 with the octet theory (pp. 488, 497) is difficult, and it must be emphasized that, in general, the co-ordination numbers of atoms provide no explanation of the nature of the linkage between the central atom and the attached groups. So many puzzling facts, however, are so beautifully correlated by the application of Werner's theory that it is now universally conceded that it must rest upon a sound basis. It constitutes, indeed, the most useful key the chemist possesses for unlocking the structure of many complex compounds, as will appear in later chapters.

Preparation of Nitrogen Tetroxide: $N_2O_4 \rightleftarrows 2NO_2$. — This substance is liberated by heating nitrates, other than those of potassium, sodium, or ammonium, such as the nitrates of lead and copper:

$$2Cu(NO_3)_2 \rightarrow 2CuO + 4NO_2 + O_2.$$

The nitrates of metals above mercury in the activity series (p. 142) leave the oxide. The nitrates of mercury and of the metals below it leave the metal. When the mixed gases are led through a **U**-tube immersed in a freezing mixture, the tetroxide condenses as a pale-yellow liquid (b.-p. 22°, m.-p. —9.3°), and the oxygen passes on.

The compound may also be made by direct union of nitric oxide and oxygen, or by oxidation of nitric oxide by concentrated nitric acid (p. 524). It is likewise almost the sole product of the interaction of *concentrated* nitric acid and copper (see p. 533).

Properties of Nitrogen Tetroxide. — The most striking peculiarity of this substance is that, when hot, it is deep brown in color, and when cold, pale yellow. The density of the almost black gas, at 156°, corresponds to the formula NO_2, that of the reddish-brown gas at 22° indicates that 90 per cent association to N_2O_4 has occurred. The darkening in color on heating is consequently due to

the progressive shift in the equilibrium $N_2O_4 \rightleftarrows 2NO_2$ towards complete dissociation of N_2O_4 as the temperature is raised (see Fig. 157).

When the temperature is carried above 156°, by passing the brown gas through a hot tube, the brown color begins to disappear again, nitric oxide and oxygen being formed. This decomposition

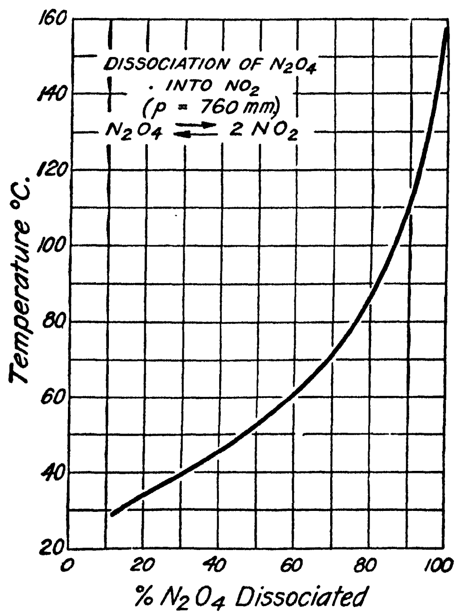


FIG. 157. Dissociation of N_2O_4 into NO_2.

is complete, however, only above 600° (see Fig. 158). On cooling, the same steps through brown to pale-yellow are retraced:

$$\underset{\text{Colorless}}{2NO + O_2} \rightleftarrows \underset{\text{Brown}}{2NO_2} \rightleftarrows \underset{\text{Pale Yellow}}{N_2O_4}.$$

The name *nitrogen peroxide* has been assigned by some chemists to the substance NO_2; it is also frequently called *nitrogen dioxide*. Both names, however, are misleading. The term *peroxide* (see page 368) implies a direct union between the oxygen atoms in the molecule, and of this there is no indication in the chemical behavior of the compound. The compound which clearly merits the title of peroxide is NO_3 (p. 523). The term *dioxide* suggests that the substance contains nitrogen in a lower state of oxidation than in the trioxide N_2O_3, whereas in point of fact the composition is intermediate between that of the trioxide N_2O_3 and that of the pentoxide N_2O_5. The name nitrogen tetroxide is thus seen to be most appropriate not only for the associated

molecule N_2O_4 (which contains four atoms of oxygen) but also for the simple molecule NO_2, in which the nitrogen atom is quadrivalent, $O = N = O$.

The electronic formula for NO_2, $:\underset{..}{\ddot{O}}:\dot{N}:\underset{..}{\ddot{O}}:$, shows that the two oxygen atoms are both linked to nitrogen by co-ordinate valences (compare SO_2, p. 490). The presence of the lone electron on the nitrogen atom is held to explain both the color of NO_2 (see p. 499) and its tendency to polymerize to form the colorless N_2O_4:

$$\begin{array}{c} :\ddot{O}:N:\ddot{O}: \\ \vdots\quad ..\quad \vdots \\ :\underset{..}{O}:N:\underset{..}{O}: \end{array}$$

Since nitrogen tetroxide yields free oxygen more readily than does nitric oxide, phosphorus burns readily in it; a taper, however, is

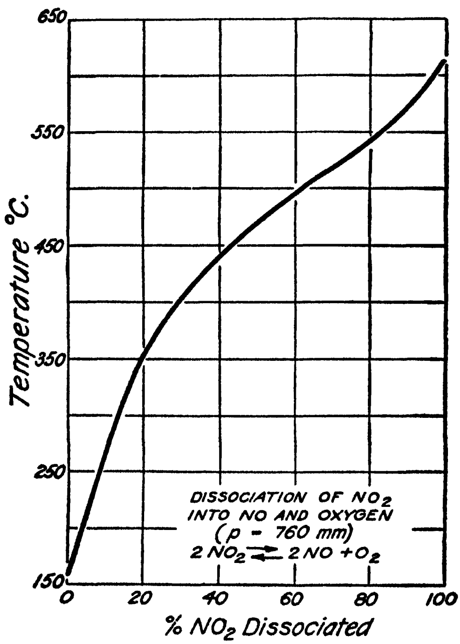


FIG. 158. Dissociation of NO_2 into NO and Oxygen.

extinguished. On account of its oxidizing power, it is sometimes used in bleaching flour.

The most interesting property of nitrogen tetroxide is its *action upon water*. The oxide is intermediate in composition between

nitrous and nitric anhydrides, and, when dissolved in *cold* water, gives *both* nitric and nitrous acids: $N_2O_4 + H_2O \rightarrow HNO_3 + HNO_2$. If a base is present, a stable mixture of the nitrate and nitrite of the metal is produced (compare p. 386). When the water is not cooled, however, the nitrous acid (p. 535), being unstable, gives nitric oxide and nitric acid, so that the final result is:

$$3NO_2 + H_2O \rightarrow 2HNO_3 + NO.$$

When excess oxygen is present also, then the NO gives more NO_2, and this in turn gives more nitric acid. This series of reactions plays an important part in the making of nitric acid from the nitrogen of the air (see next section).

Fixation of Atmospheric Nitrogen. The Arc Process. — Oxygen and nitrogen have no natural tendency to combine at the ordinary temperature, but rather the reverse — their compounds tend to decompose with evolution of heat. But a high temperature will supply the necessary energy. Even so, however, the union extends to only 1 per cent of the mixture at 2000° and 5 per cent at 3000°:

$$N_2 + O_2 + 43{,}200 \text{ calories} \rightleftarrows 2NO.$$

Note that, since the formation of NO is an endothermic reaction, the yield of NO is *increased* by raising the temperature (Van't Hoff's law, p. 284. In spite of the poor yield obtainable under the best conditions, the supply of natural nitrates is so limited that machinery has been devised, and was for some years in extensive use until more efficient and cheaper methods of nitrogen fixation (pp. 507, 734) were perfected, for carrying on the combination on a commercial scale. The present survival of the process is dependent upon the availability of cheap hydro-electric power.

In the **Birkeland-Eyde process,** still used at Notodden and elsewhere in Norway, an arc discharge between water-cooled copper poles is spread, by the influence of powerful electromagnets, into a circular brush discharge several feet in diameter, the temperature of which is about 3000°. Air is blown through the flame, giving a mixture of gases containing about 1 per cent of NO, and this is quickly cooled to permit of union of the nitric oxide with oxygen, to give the tetroxide NO_2. The air containing NO_2 is then passed through absorbing towers down which water trickles. Here the action mentioned in the last section takes place, and an aqueous

solution of nitric acid is produced. In peace times, the nitric acid is mixed with calcium hydroxide (slaked lime):

$$Ca(OH)_2 + 2HNO_3 \rightarrow Ca(NO_3)_2 + 2H_2O$$

to give calcium nitrate, which is sold as a fertilizer. In war times, the acid is concentrated for the manufacture of explosives by addition of concentrated sulphuric acid (p. 427) and distillation.

Nitric Acid from Ammonia. — The *ammonia oxidation* process (Ostwald) for the production of nitric acid was developed on a large scale during the Great War, particularly in Germany. Gaseous ammonia heated with oxygen in the presence of a suitable catalyst undergoes oxidation, with the formation of oxides of nitrogen and water vapor. The oxides of nitrogen can be recovered by absorption in water, yielding dilute nitric acid. This can be concentrated further if desired, or neutralized with a base for the production of nitrates for use as explosives (ammonium nitrate) or fertilizers (calcium nitrate).

Platinum gauze is almost universally employed as a catalyst. A mixture of ammonia and oxygen-enriched air passes through one or more layers of the gauze, which is heated electrically to 650°–700° to start the reaction and is maintained at that temperature subsequently by the heat of combustion of the ammonia. The reaction that takes place may be represented by the equation:

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O.$$

The excess oxygen present converts the NO into NO_2 as the issuing gases cool. Unless the reaction is very nicely regulated, however, the yield of oxides of nitrogen is diminished either by incomplete combustion of ammonia, or by the dissociation of NO into nitrogen and oxygen (see p. 530). The time of contact with the catalyst must not be too long, or this latter effect will be appreciable. With proper precautions, a conversion efficiency of 95–98 per cent is obtained. *Poisoning of the catalyst* must be guarded against by careful purification of the gases, especially from non-volatile impurities such as dust particles, which choke the surface of the gauze and render it inoperative.

A new platinum gauze is perfectly smooth, and incidentally is not a very efficient catalyst. After it has been in use for some time, however, the gauze appears quite differently under the microscope. It is still metallic platinum,

but its surface is now covered with minute craters, and is efficiency is remarkably increased. If properly cared for and kept free from *poisons,* 2 gauzes each one square foot in area will suffice for the production of 1.5 to 1.8 metric tons of 100 per cent nitric acid per 24 hours for three months or longer.

Oxidizing Actions of Nitric Acid

When nitric acid gives up oxygen to any substance, it is itself reduced. Hence, according to convenience, we shall refer to oxidations by, or reductions of, nitric acid.

Oxidation of Hydrogen. — The metals preceding hydrogen in the electromotive series (p. 313) displace hydrogen-ion from nitric acid in aqueous solution, as they do from other acids. With metals more active than zinc, such as magnesium, a great part of the hydrogen escapes in the free condition. But, in the case of zinc and the metals below it, most or all of the hydrogen is oxidized to water by the nitric acid, and part of the acid is reduced. Thus with zinc and *very dilute* nitric acid, almost the only product, aside from zinc nitrate, is ammonia. This interacts with the excess of nitric acid present to form ammonium nitrate:

$$4Zn + 10HNO_3 \rightarrow 4Zn(NO_3)_2 + NH_4NO_3 + 3H_2O.$$

The student will find it very instructive to derive this balanced equation from its skeleton: $Zn + HNO_3 \rightarrow Zn(NO_3)_2 + NH_4NO_3 + H_2O$, using the valence method described on p. 378. Simpler, and of still greater value for the complete understanding of this and similar reactions presented immediately below, is the balancing of the equation by the use of ions and electrons, as discussed on p. 379.

Heavy Metals. — The less active metals, such as copper and silver, do not displace hydrogen from dilute acids (p. 142), but reduce nitric acid, nevertheless, and are converted into nitrates. Platinum and gold (compare p. 427) alone are not attacked. Thus copper, with somewhat *diluted* nitric acid (sp. gr. 1.2), gives cupric nitrate and nitric oxide NO:

$$8HNO_3 + 3Cu \rightarrow 4H_2O + 2NO + 3Cu(NO_3)_2.$$

The nitric oxide is liberated as a colorless gas, but forms the brown tetroxide at once on meeting the oxygen of the air (p. 524).

When *concentrated* nitric acid is used with copper, almost pure nitrogen tetroxide is obtained:

$$4HNO_3 + Cu \rightarrow 2H_2O + 2NO_2 + Cu(NO_3)_2.$$

The above are simple types of the interactions of metals with nitric acid. In actual experiments the behavior is usually more complex (see, for example, tin, p. 823). As a rule, the action is very slow at first, and gathers speed with the accumulation of the reduction products, which act catalytically. Intermediate concentrations of nitric acid act upon metals to give *mixtures* of the two oxides, and, with zinc, even nitrous oxide N_2O and nitrogen may be found in considerable quantities in the gases evolved.

Oxidation of Non-Metals. — With non-metals the actions are different, in so far that these elements form no nitrates. Thus sulphur boiled in nitric acid gives sulphuric acid, along with nitric oxide, equation (1), or with nitrogen tetroxide, equation (2), or with both (concurrent reactions, p. 388), according to the concentration of the acid:

$$2HNO_3 + S \rightarrow 2NO + H_2SO_4. \quad (1)$$
$$6HNO_3 + S \rightarrow 6NO_2 + 2H_2O + H_2SO_4. \quad (2)$$

The reader should note the constant production of **nitric oxide with diluted nitric acid,** and the invariable formation of **nitrogen tetroxide with concentrated acid.** This is explained by the fact that nitrogen tetroxide cannot pass unchanged through a liquid containing much water, for it gives nitric acid and nitric oxide with the latter (p. 530). Conversely, where the nitric acid is concentrated, nitric oxide, even if formed by the interaction with the metal, must be oxidized to nitrogen tetroxide as it passes up through the liquid (p. 524).

Oxidation of Compounds: Aqua Regia. — Compounds also like hydrogen sulphide and sulphurous acid, which are easily oxidized, interact readily with nitric acid. With diluted nitric acid, the products are free sulphur and sulphuric acid respectively.

Even hydrochloric acid, which is not affected by oxidizing agents such as hydrogen peroxide or concentrated sulphuric acid, is oxidized by concentrated nitric acid.* Besides free chlorine, nitrosyl chloride NOCl is formed. The mixture of nitric acid and hydrochloric acid is known as *aqua regia.* It is frequently used in analysis, for example, to oxidize sulphur (say, in cast iron or in min-

* A new method for the commercial production of chlorine makes use of this reaction. Sodium chloride is treated with concentrated nitric acid, the oxides of nitrogen evolved with the chlorine are reconverted to HNO_3, and sodium nitrate is obtained as a by-product.

erals), the sulphuric acid formed being estimated by precipitation and weighing of barium sulphate (p. 428).

Aqua regia (Latin, *royal water*) received its name because it converts the "noble" metals, gold and platinum, into soluble compounds. This it does because the chloride ion, in presence of an oxidizing agent such as nitric acid, combines with the metals to form exceedingly stable complex ions, $AuCl_4^-$, the negative ion of chlorauric acid (see p. 813), and $PtCl_6^=$, the negative ion of chloroplatinic acid (see p. 817). In the case of gold:

$$Au + 4Cl^- \rightarrow AuCl_4^- + 3\ominus$$
$$3NO_3 + 6H^+ + 3\ominus \rightarrow 3NO_2 + 3H_2O$$

Adding: $Au + 4Cl^- + 3NO_3^- + 6H^+ \rightarrow AuCl_4^- + 3NO_2 + 3H_2O$

In full: $Au + 4HCl + 3HNO_3 \rightarrow HAuCl_4 + 3NO_2 + 3H_2O$

The idea that a nascent form of chlorine exists here is even more superfluous than is the similar assumption about oxygen (p. 246).

So-called "Nascent" Hydrogen.—It will be profitable to consider briefly, at this point, some reactions in which the introduction of this term has caused considerable confusion in the past.

When hydrogen gas is led through cold nitric acid, little or no action occurs. But hydrogen adsorbed on platinum or palladium (p. 139), or liberated by electrolysis on electrodes made of these metals, reduces nitric acid readily. Many metals have, in a greater or less degree, this power of increasing the activity of hydrogen. Thus the iron-molybdenum catalyst in the Haber process (p. 507) facilitates the union of hydrogen and nitrogen to form ammonia. Other elements, such as the oxygen in the contact sulphuric acid process (p. 419), are also rendered more active by contact agents like platinum.

This more **active state** of hydrogen is certainly connected with a change in the chemical unit, or molecule, and it seems most plausible to assume that it is due to the formation of **atomic hydrogen.** Thus, to return to the Haber process for the purpose of illustration, it is known that iron forms a very unstable compound with hydrogen—a *hydride* (p. 450). Molybdenum forms a very unstable compound with nitrogen—a *nitride* (p. 505). Alone, each metal is a comparatively poor catalyst. The simplest way in which we can visualize the vastly superior efficiency of the mixture is that simultaneous decomposition of unstable hydride and unstable nitride releases hydrogen and nitrogen atoms in close proximity, and rapid formation of NH_3 is thereby promoted.

The dissociation of the hydrogen molecule into its simple atoms, it should be mentioned, is a highly endothermic reaction (see p. 510), so that atomic hydrogen brings a great deal more energy to a reduction than does molecular hydrogen, just as ozone brings more energy to oxidation than does oxygen (p. 365). The greater activity is thus a natural consequence of this difference in available energy.

Unfortunately the more active state of hydrogen is frequently described as the **nascent state,** because it happens that reductions can often be brought

about in the presence of substances which normally produce hydrogen that do not occur in the presence of free hydrogen. Thus in the presence of tin and hydrochloric acid (p. 516), nitric acid is reduced to hydroxylamine, although (as we have noted above) free hydrogen has practically no effect on cold nitric acid. The idea behind the term "nascent hydrogen" as an explanation for the reduction which occurs in such cases is exactly similar to that behind the term "nascent oxygen," discussed in detail on p. 246, and equally cogent arguments against the validity of the idea may here be adduced.

This form of hydrogen has never been observed or isolated as a substance. If it is an allotropic form, its degree of activity should be defined quantitatively. In point of fact, however, concentrated sulphuric acid gives, with copper, sulphur dioxide (p. 415), and with zinc, hydrogen sulphide (p. 133), so that the nascent hydrogen (if *it* is the active agent) is much more active in the second case. Again, hydrochloric acid and dilute nitric acid, with zinc, give ammonia (p. 532), with magnesium no ammonia, with tin a mixture of ammonia and hydroxylamine (p. 516). The logical explanation of such differences in behavior is to be found in a study of the **oxidation-reduction reactions and the various energy changes which they involve.** For a full discussion of these latter, the reader is referred to a textbook in physical chemistry, although a brief exposition of certain points will be found in the chapter on Electromotive Chemistry (Chapter XLIX).

Nitrous Acid, Hyponitrous Acid, and their Anhydrides

Nitrites and Nitrous Acid. — When the nitrates of potassium and sodium are heated, they lose one unit of oxygen, and the **nitrites** remain:

$$2NaNO_3 \rightarrow 2NaNO_2 + O_2.$$

Commonly lead is stirred with the melted nitrate and assists in the removal of the oxygen. The litharge PbO which is formed remains as a residue when the sodium nitrite is dissolved for recrystallization.

When an acid is added to a *dilute* solution of a nitrite, a pale-blue solution containing **nitrous acid** HNO_2 is obtained. The acid is very unstable, however, and, when the solution is warmed, it decomposes:

$$3HNO_2 \rightarrow HNO_3 + 2NO + H_2O.$$

When a *concentrated* solution of sodium nitrite is acidified, the nitrous acid formed decomposes at once, and a brown gas containing the anhydride escapes:

$$2H^+ + 2NO_2^- \leftrightarrows 2HNO_2 \leftrightarrows H_2O + N_2O_3 \uparrow.$$

This behavior distinguishes a nitrite from a nitrate.

Nitrous acid is an active oxidizing agent:

$$2HI + 2HNO_2 \rightarrow 2H_2O + 2NO + I_2.$$

Indigo is also converted by it into isatin (compare p. 365). On the other hand, oxidizing agents which are sufficiently active, like acidified potassium permanganate, convert nitrous acid into nitric acid:

$$3H_2SO_4+2KMnO_4+5HNO_2 \rightarrow K_2SO_4+2MnSO_4+3H_2O+5HNO_3.$$

Nitrous acid is much used in the making of organic dyes.

Nitrous Anhydride N_2O_3. — A study of the density of the gas arising from the decomposition of nitrous acid shows that, in the gaseous state, the anhydride is almost entirely dissociated:

$$N_2O_3 \rightleftarrows NO + NO_2.$$

When the mixture is led through a **U**-tube immersed in a freezing mixture at —21°, a deep-blue liquid is obtained which is the anhydride itself. This dissociates rapidly when allowed to boil.

The same equilibrium mixture of the three gases is obtained by the action of water on nitrosylsulphuric acid (p. 422).

Hyponitrous Acid $H_2N_2O_2$. — This acid is formed by the interaction of hydroxylamine and nitrous acid in aqueous solution:

$$H-O-N\boxed{H_2 + O}N-O-H \rightarrow H_2O + H-O-N=N-O-H.$$

With nitrate of silver, the yellow, insoluble silver hyponitrite $Ag_2N_2O_2$ is precipitated. When this salt is shaken with an ethereal solution of hydrogen chloride, the acid is liberated, and the insoluble silver chloride may be separated by filtration. Finally, evaporation of the ethereal solution leaves hyponitrous acid as a white solid. It explodes when heated, and its solution in water is an exceedingly feeble acid. The warm aqueous solution decomposes slowly, giving nitrous oxide:

$$H_2N_2O_2 \rightarrow H_2O + N_2O.$$

and this change is *not* capable of reversal.

Nitrous Oxide N_2O. — Nitrous oxide is prepared by gently heating ammonium nitrate (great care should be taken; see next page), or a solution of a salt of ammonium and a nitrate:

$$NH_4^+ + NO_3^- \rightleftarrows NH_4NO_3 \rightarrow 2H_2O + N_2O.$$

The steam condenses, and the nitrous oxide may be collected over warm water, or be dried and compressed into steel cylinders.

Its solubility in cold water is considerable: at 0°, 130 volumes in 100; at 25°, 60 in 100. The liquefied gas boils at —89.8° and its vapor tension at 20° is 49.4 atmospheres.

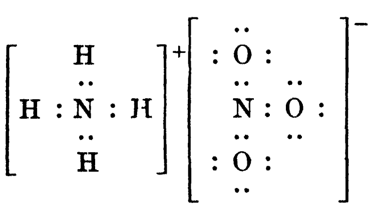
A glowing splinter of wood bursts into flame in nitrous oxide, and phosphorus and sulphur burn in it with much the same vigor as in oxygen. In all cases oxides are formed, and nitrogen is set free. It does not combine with nitric oxide, however, as does oxygen (p. 524).

Metals do not rust in nitrous oxide, and the hæmoglobin of the blood is unable to use it as a source of oxygen. It is employed as an anæsthetic for minor operations. The hysterical symptoms which accompany its use caused it to receive the name of "laughing gas."

Graphic Formulæ of Nitric Acid and its Derivatives: Explosives. — While concentrated nitric acid is regarded as a complex equilibrium mixture of several types of molecule:

$$HO.NO_2 \rightleftarrows [H_3O][NO_3] \rightleftarrows [(HO)_3N][NO_3]_2,$$

the only significant products in dilute aqueous solution are the ions H^+ (or H_3O^+, see p. 340) and NO_3^-. When the acid is neutralized by bases, the negative ion NO_3^- also exists in the salts which are formed. The electronic formula for ammonium nitrate, for example, is represented thus:



This structural formula of ammonium nitrate serves to explain the fact that the salt is able to exist at all, by representing the oxygen and hydrogen as being separated from one another and at-

tached to different nitrogen units. When the equilibrium of the system is disturbed by heating, the oxygen and hydrogen unite to form water, an arrangement which is much more stable, and nitrous oxide (p. 537) escapes with the steam. The behavior of ammonium nitrite on heating (p. 505) is explained in the same way.

It may be noted that the reaction $NH_4NO_3 \rightarrow 2H_2O + N_2O$ is accompanied by the evolution of 9000 calories of heat. This is not an excessively exothermic reaction, but if care is not taken a serious explosion is liable to result when ammonium nitrate is heated, for the compound N_2O itself decomposes into its elements at higher temperatures, and the reaction $2N_2O \rightarrow 2N_2 + O_2$ evolves an additional 38,000 calories. The final products of the decomposition of ammonium nitrate are therefore nitrogen, oxygen and water vapor, and if the decomposition is brought about suddenly these three substances, as gases, will occupy at the high temperature to which they are raised by the heat of the above reactions a volume out of all proportion to the small quantity of solid substance from which they were produced.

It is these same two factors — the endothermal character of the compounds, and their ready decomposition into simpler gaseous substances — that render many organic derivatives of nitric acid both useful and terrible as **explosives** (see Chapter XXXVIII).

On the morning of Sept. 21, 1921, a terrific explosion occurred in that portion of the Oppau plant of the Badische Anilin and Soda Fabrik devoted to the production of ammonium nitrate and other salts. The buildings concerned disappeared entirely and not one of the workmen in or near them escaped. A mammoth crater, 250 feet in diameter and more than 50 feet deep, was formed in the earth. 430 lives were lost and nearly $50,000,000 worth of property was destroyed. The sound of the explosion and the earth shocks reached as far as Bayreuth, 145 miles distant, and the air pressure wave caused considerable damage in Frankfort, 53 miles away. The exact cause of the disaster will probably never be determined.

Exercises. — 1. Make the equation for the interaction of ferrous chloride, hydrochloric acid, and nitric acid (p. 523), and for all the actions concerned when the test for a nitrate (p. 524) is applied to sodium nitrate. What volume (at 0° and 760 mm.) of NO is obtained from one formula-weight of nitric acid?

2. In the action of zinc on dilute nitric acid (p. 532), why is not the ammonia given off as a gas? How should you show that it was formed at all?

3. Make ion-electron equations for the formation of nitric oxide and nitrogen tetroxide by the action of carbon on nitric acid (p. 533).

4. Make ion-electron equations for the interaction of iron with diluted and with concentrated nitric acid, respectively (pp. 532–3). The iron gives ferric nitrate $Fe(NO_3)_3$.

5. Give the three ways in which nitrates decompose when heated, with one equation illustrating each.

6. Make all the equations for oxidations on pp. 532–3, using the methods illustrated on pp. 378–9.

7. How could you distinguish nitric oxide, (*a*) from hydrogen, (*b*) from oxygen?

8. Justify the nomenclature in the case of the oxides and oxygen acids of nitrogen (pp. 383, 520). Why is it incorrect to call NO_2 nitrogen peroxide (p. 528)?

9. To 10 c.c. of a 0.5 *N* solution of nitric acid, excess ferrous sulphate and sulphuric acid are added, and the mixture boiled. What is the volume of nitric oxide evolved?

10. 25 c.c. of the colorless gas obtained by the action of copper on dilute HNO_3 are collected in a 50 c.c. graduated cylinder over water. 25 c.c. of oxygen are collected in a second graduated cylinder. By inverting the second cylinder under the first in a trough, the contents of the two are mixed. What do you observe? What volume of what gas remains? Explain.

11. What will be the volume occupied by 1 g. mol. wt. of N_2O_4 when heated to (*a*) 156°, (*b*) 650°, under one atmosphere pressure. Use Figs. 157 and 158.

12. At 52° and 760 mm., N_2O_4 is 50 per cent dissociated into NO_2 (see Fig. 157). What is the vapor density, on the basis $O_2 = 32$?

13. At 470° and 760 mm., NO_2 is 50 per cent dissociated into nitric oxide and oxygen (see Fig. 158). What is the vapor density on the basis $O_2 = 32$?

14. What would be the effect of increased pressure upon the following equilibria: (*a*) $N_2O_4 \rightleftarrows 2NO_2$; (*b*) $2NO_2 \rightleftarrows 2NO + O_2$; (*c*) $N_2 + O_2 \rightleftarrows 2NO$? What law do you apply?

15. How could you prove that the forward reactions in (*a*) and (*b*) of the preceding exercise are endothermic, without actually measuring the heats of reaction? What law do you apply?

16. Explain why the temperature maintained by the gauze in the ammonia oxidation process (p. 531) depends upon the oxygen content of the air which is mixed with the ammonia (p. 100).

17. Give two methods for the preparation of sodium nitrite, with equations.

18. Analyze and balance the following skeleton equations by the ion and electron method:

(*a*) $HI + HNO_2 \rightarrow I_2 + NO + H_2O$.
(*b*) $KMnO_4 + H_2SO_4 + KNO_2 \rightarrow K_2SO_4 + MnSO_4 + HNO_3 + H_2O$.

19. What will be the volume of gases produced by the explosion of 10 g. of ammonium nitrate, assuming the products to be at 500° and 760 mm. pressure?

20. Write the electronic formulæ of the following substances: (*a*) ammonium sulphate, (*b*) ammonium nitrite, (*c*) nitrogen pentoxide N_2O_5.

21. Should you classify as molecular compounds (p. 524): Chlorine hydrate, ammonium hydroxide, KI_3 (p. 350), sulphurous acid, sodium tetrasulphide (p. 411)? Attempt to justify your answer in each case.

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CHAPTER XXXI

PHOSPHORUS

There are many things in the chemistry of phosphorus and its compounds which remind us of nitrogen. Yet these are largely referable to the fact that the elements are both non-metals and both have the same main valences, *viz.*, three and five. The behavior of the compounds is often very different. For the present it is sufficient to say that both give compounds with hydrogen, NH_3 and PH_3, and both yield oxides of the forms X_2O_3, X_2O_4, and X_2O_5. The first and last of these oxides are acid-forming, and phosphorus, therefore, gives acids corresponding to nitrous and nitric acids. The element is thus a non-metal.

Occurrence. — Phosphorus is found in nature in the form of phosphates. Calcium phosphate $Ca_3(PO_4)_2$ forms 26 per cent of the bones and teeth of animals, and it occurs in all fertile soils. It constitutes a large part of the "phosphate rock" of Georgia, Florida, the Carolinas, Tennessee, and of Algeria and Tunis. Complex organic compounds of phosphorus, such as lecithin, are essential constituents of the muscles, nerves and brains of animals and are found also in plants. The average man's skeleton contains 1400 g. of phosphorus, his muscles 130 g., and his nerves and brain 12 g. Amongst foods, egg-yolks and beans contain an unusually large proportion, nuts, peas, and wheat (entire grain) coming next.

Phosphorus was discovered by Brand in 1669, and by Kunkel in 1670, by distilling at a white heat the solid residue from evaporated urine. They were both searching for the philosopher's stone. Scheele in Sweden prepared it from bones in 1771.

Manufacture of Phosphorus. — Phosphorus is now manufactured from natural calcium phosphate. This is pulverized and mixed with the proper proportions of carbon and silicon dioxide (sand), and the mixture is introduced continuously into an electric furnace (Fig. 159), entering at the top *B* through a worm feed *A*. The discharge of an alternating current between carbon poles *C* and

C produces the very high temperature which the action requires. The calcium silicate which is formed fuses to a slag, and can be withdrawn at intervals through a pipe *D* at the bottom of the furnace. The gaseous products distil off through a pipe *E* and the phosphorus is condensed by means of cold water:

$$Ca_3(PO_4)_2 + 3SiO_2 + 5C \rightarrow 3CaSiO_3 + 5CO + 2P.$$

We may regard the phosphate as being composed of two oxides, $3CaO,P_2O_5$. It thus appears that the calcium oxide has united with the silica, which is an acid anhydride (see p. 661): $CaO + SiO_2 \rightarrow CaSiO_3$, while the phosphoric anhydride has been reduced.

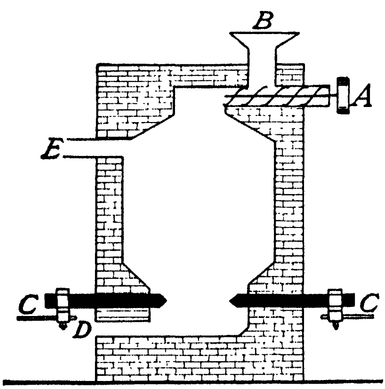


FIG. 159. Manufacture of Phosphorus.

The phosphorus, after purification, is cast into sticks in tubes of tin or glass, standing in cold water.

Physical Properties. — There are several allotropic forms (p. 365) of phosphorus, the two most familiar being known commonly as white phosphorus and red phosphorus. **White phosphorus,** prepared as described above, is at first transparent and colorless, but after exposure to light acquires a superficial coating of the red variety. On account of the yellow tint which ordinary samples thus exhibit, it is frequently called *yellow phosphorus*. It melts at 44° and boils at 280°. Its sp. gr. is 1.83. The mol. wt. of its vapor at 313° is 128 and the formula, therefore, P_4. White phosphorus is soluble in carbon disulphide, less soluble in ether, and insoluble in water. It is exceedingly poisonous, less than 0.15 g. being a fatal dose, and is an ingredient in roach-paste and rat poison. Continued exposure to its vapor causes necrosis, a disease from which match-makers are apt to suffer. The jaw-bones and teeth are particularly liable to attack.

Red phosphorus is a red powder consisting in part of small tabular crystals. It is obtained by heating white phosphorus to about 250° in a vessel from which air is excluded. A trace of iodine accelerates the transformation, and it then takes place even in the cold.

Red phosphorus sublimes before melting when heated under atmospheric pressure. Its vapor is identical with that of white phosphorus, and condenses to that form, indeed, when suddenly cooled (as in distillation). It is insoluble in carbon disulphide and other solvents. It is not poisonous, and, unlike white phosphorus, does not require to be kept under water to avoid spontaneous combustion. Its melting-point, obtained by heating in a closed vessel under excess pressure, varies, being 550° when heated very slowly, and 600° when heated rapidly. Certain other of its properties are variable, *e.g.*, density from 2.05 to 2.34. Bridgman, by heating white phosphorus at 200° under a pressure of 1200 kg. per sq. cm., has recently obtained **black phosphorus** (sp. gr. 2.69). A second white modification also exists at very low temperatures.

Chemical Properties of White Phosphorus. — **White phosphorus** unites directly with the halogens with great vigor. It unites slowly with oxygen in the cold, and with sulphur and many metals when the materials are heated together. The slow union of *cold* phosphorus with atmospheric oxygen is accompanied by the evolution of light. Hence the word phosphorescence. The name of the element (Greek φῶς, light; φέρω, I bear) records this property. Apparently the chemical energy, transformed in connection with the oxidation, is converted, in part at least, into radiant energy instead of completely into heat.* The slow oxidation of phosphorus is accompanied by the production of ozone, but the nature of the action is still unknown (see p. 363).

When phosphorus burns in *perfectly dry* air, the cloud of solid pentoxide particles very quickly subsides. When phosphorus burns in *moist* air, however, the cloud of pentoxide forms tiny droplets, consisting of a concentrated solution of phosphoric acid, which remain suspended in the atmosphere as a *fog* (compare sulphur trioxide, p. 421). Burning phosphorus was therefore used in the war for screening the movement of vessels. In land warfare, shells containing white phosphorus were also employed for incendiary purposes. Such shells produced horrible, and usually fatal, burns on any enemy within the radius of their explosion.

The phenomenon of **phosphorescence** is rather puzzling in some of its aspects. In *pure oxygen* under 760 mm. pressure, white phosphorus does not glow unless the temperature is raised to 27°. At ordinary temperatures, the

* The same production of light from chemical action in a cold body is seen in the luminosity of certain parts of fireflies and some species of fish.

glow appears only when the oxygen pressure is reduced to about 200 mm., either by partial evacuation or by addition of an inert gas (such as nitrogen in air). At lower temperatures, the partial pressure of oxygen must be still further decreased before phosphorescence is in evidence.

This seems strange, since it will be recalled how frequently we have preached the law of molecular concentration (p. 272) and its applications. One would think that phosphorus ought to oxidize more rapidly in pure oxygen than in air. Why, then, does it not phosphoresce? Because the phosphorescence is due not to phosphorus itself, but to an intermediate oxide P_2O_3. If there is plenty of oxygen present, this is oxidized right on to P_2O_5 as rapidly as it forms. If the local supply of oxygen is less abundant, however, than the P_2O_3 gets an opportunity to let its light shine before it passes on its way to P_2O_5. Compare the time reaction on p. 389.

Chemical Properties of Red Phosphorus. — This variety of the element, since its formation from the white modification involves evolution of heat, contains less energy than does white phosphorus and is much less active. It does not catch fire in the air below 240°, while ordinary phosphorus ignites at 35–45°. Indeed, it is the vapor that begins to combine with oxygen, and this behavior is only an independent proof of the low vapor tension of the red variety. When the vapor tension of white phosphorus has reached 760 mm. (at 280°, the b.-p.), that of red phosphorus is almost imperceptible.

Red phosphorus is to be regarded as the normal, stable form of phosphorus. The fact that white phosphorus can be kept a great length of time, and is changed but slowly on exposure to light, only shows that the transformation into a more stable condition is retarded by the lowness of the temperature (compare p. 282).

The relation between the two varieties of phosphorus is quite distinct from that between rhombic and monoclinic sulphur (p. 399). In the latter case there is a definite temperature of transformation (96°) above which one form completely disappears, and below which the other form is incapable of permanent existence. With the varieties of phosphorus no such point of transformation exists. It is only by condensing the vapor that the white kind is obtained.

Substances like sulphur, where the two forms exhibit a definite transition point, are termed **enantiotropic**; substances like phosphorus and carbon (p. 559), where no transition point exists, are called **monotropic.**

The Principle of Transformation by Steps. — It may have occurred to the reader as strange that it should be possible to make white phosphorus by distilling red phosphorus (p. 543) when the product undergoes the reverse transformation spontaneously, even when kept in the cold. How can a substance be formed under certain conditions, when under the same or, even, under more favor-

able conditions it proves to be incapable of continued existence? We should expect rather that obtaining the products of its decomposition would have been the only result of the effort to make it.

Extraordinary as this fact appears to be, it is nevertheless very commonly encountered. Perchloric acid (p. 387) and nitric anhydride (p. 522) are made by distillation and afterwards break up of their own accord. So, also, hypochlorites are formed first and can be isolated. But under the same conditions the further transformation to chlorates will occur (p. 384). A simple case is that of sulphur made by precipitation (p. 432) at the ordinary temperature. Although it is naturally solid below 114°, yet when first thrown down, it is in the form of liquid droplets which, if undisturbed, may remain fluid for weeks. Similarly, sulphur vapor condenses on glass in drops which remain liquid for years, unless they are touched or rubbed. Finally, a supersaturated solution (p. 208) is not unlike cold liquid sulphur.

In all these cases there is a possibility of further change, which, when it comes, will liberate heat or some other form of energy. Thus, heat is set free when the liquid sulphur is precipitated. The amount of heat would have been greater, by the heat of fusion of the sulphur, if solidification had occurred simultaneously. But, in spite of the existence of this justification for the final step, this step is not taken. So, the decomposition of the vapor of the perchloric acid or of the nitric anhydride would have added to the amount of energy liberated as heat, but this additional step was postponed. In other words, **transformations which proceed spontaneously** and with evolution of heat, **may go forward by steps, when there are intermediate substances,** or allotropic forms, **capable of existence.** This is known as the **principle of transformation by steps,** and was first formulated by Ostwald.

Uses of Phosphorus, Matches. — The greater part of the phosphorus of commerce is employed in the manufacture of matches. The first articles of this sort (1812) were sticks coated with sulphur and tipped with a mixture of potassium chlorate and sugar. For ignition they were dipped into a bottle containing asbestos moistened with concentrated sulphuric acid. Matches involving the use of phosphorus (1827) have now displaced all others. These are of two kinds, ordinary matches, which strike on any rough surface, and "safety" matches. Ordinary matches are still made in some countries by dipping the splints of wood in melted paraffin, and then in a paste made of 4 to 7 per cent of white phosphorus, lead dioxide

about 50 per cent, water, and dextrin (paste). The head, when dry, is dipped in varnish to exclude air and moisture. Where the use of white phosphorus is very properly forbidden, a sulphide P_4S_3 is substituted. When the match is struck, the friction explodes the mixture of phosphorus trisulphide (combustible) and lead dioxide (or other oxidizing agent), and the resulting heat sets fire to the paraffin and this, in turn, to the wood.

Safety matches carry no phosphorus, but only a mixture of substances containing oxygen, such as potassium chlorate or potassium chromate, with a combustible, like antimony trisulphide, some dextrin and a filling (*e.g.*, chalk). The box is coated with a mixture of red phosphorus, antimony trisulphide, dextrin and filling. The friction converts a trace of the red phosphorus into the white variety, and the latter sets fire to the head. To prevent smoldering of the burned matches, the upper ends of the sticks are sometimes soaked in a solution of alum or sodium phosphate.

Phosphine. — Three hydrides of phosphorus are known. These are, phosphine PH_3 (a gas), a liquid hydride P_2H_4, which is presumably the analogue of hydrazine (N_2H_4), and a solid hydride P_4H_2.

Phosphine PH_3 cannot be made by direct union of its elements. It is, however, readily prepared by boiling white phosphorus with potassium hydroxide solution in a flask provided with a delivery tube (Fig. 160). Potassium hypophosphite is formed at the same time:

$$3KOH + 4P + 3H_2O \rightarrow 3KH_2PO_2 + PH_3\uparrow .$$

The gas made in this way contains a little of the vapor of the liquid hydride, which is spontaneously inflammable, and consequently the bubbles of the mixture catch fire when they reach the surface of water in the trough: $PH_3 + 2O_2 \rightarrow H_3PO_4$. In still, moist air, the fog of droplets of phosphoric acid solution forms beautiful smoke rings. It is necessary to pass a current of illuminating gas, nitrogen or some other inert gas through the flask by means of a second glass tube (afterwards closed with a clip, see Fig. 160) for a few minutes before starting to heat, in order to displace all the oxygen inside the flask.

A simpler method of preparing phosphine is by the action of water upon calcium phosphide:

$$Ca_3P_2 + 6H_2O \rightarrow 3Ca(OH)_2 + 2PH_3.$$

This action is analogous to that of water upon magnesium nitride (p. 505), by which ammonia is produced. In consequence of the fact that commercial calcium phosphide is a material of irregular composition, a mixture of all three hydrides is generally obtained. By passing the gas through a strongly cooled delivery tube, however, the other compounds are condensed and fairly pure phosphine passes on.

Phosphine is a colorless gas, which is easily decomposed by heat into its elements. It is exceedingly poisonous and, unlike ammonia, it is insoluble in water, and furnishes no basic compound

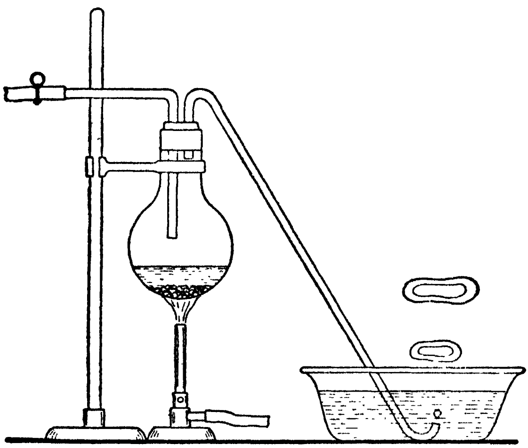


FIG. 160. Preparation of Phosphine.

corresponding to ammonium hydroxide. It resembles ammonia, formally at least, in uniting with the hydrogen halides (see below). It differs from ammonia, however, inasmuch as it does not unite with the oxygen acids. Phosphine acts upon solutions of some salts, precipitating phosphides of the metals:

$$3CuSO_4 + 2PH_3 \rightarrow Cu_3P_2 \downarrow + 3H_2SO_4.$$

Shells containing metallic phosphides are of service in naval warfare as *markers* in night engagements, the impure phosphine produced by the action of the water on the phosphides burning spontaneously on the surface and indicating the position of the shot.

Phosphonium Compounds. — Hydrogen iodide unites with phosphine to form a colorless solid, crystallizing in beautiful, highly refracting, square prisms: $PH_3 + HI \rightarrow PH_4I$. Hydrogen chloride

combines similarly with phosphine, but only when the gases are cooled by a freezing mixture, or are brought together under a total pressure of 18 atmospheres at 14°. When the pressure is released, rapid dissociation occurs. This dissociation is one of the many cases where an action which absorbs heat, nevertheless goes on spontaneously (see p. 258). The indispensable fall in the energy of the system takes place by virtue of the expansion of the constituents, and in amount this more than offsets the heat acquired.

In imitation of the ammonia nomenclature, these substances are called **phosphonium iodide** and **phosphonium chloride** PH_4Cl. They are entirely different, however, from the corresponding ammonium derivatives, for they do not give the PH_4^+ ion in aqueous solution. When brought in contact with water, they decompose into their constituents, the hydrogen halide going into solution, and the phosphine being liberated as a gas.

Halides of Phosphorus. — The existence of the following halides has been proved conclusively:

....	....	....	P_2I_4 (solid)
PF_3 (gas)	PCl_3 (liquid)	PBr_3 (liquid)	PI_3 (solid)
PF_5 (gas)	PCl_5 (solid)	PBr_5 (solid)	....

These substances may all be formed by direct union of the elements. They are incomparably more stable than are the similar compounds of nitrogen. They are all completely hydrolyzed by water, and each gives an oxygen acid of phosphorus and the hydrogen halide (see below). This action was used in the preparation of hydrogen bromide (p. 346) and hydrogen iodide (p. 352).

Phosphorus trichloride PCl_3 is made by passing chlorine gas over melted phosphorus in a flask until the proper gain in weight has occurred. The substance, a liquid boiling at 76°, is stable (see p. 173). When excess of chlorine is employed, **phosphorus pentachloride** PCl_5, a white solid body, is formed. When moist air is blown over any of these substances, the water is condensed to a fog by the hydrogen halide. In the case of the interaction of the pentachloride and water, phosphoric acid is formed:

$$PCl_5 + 4H_2O \rightarrow H_3PO_4 + 5HCl.$$

With a limited supply of water the hydrolysis is not so complete, and phosphoryl chloride * (phosphorus oxychloride), a liquid boiling at 107°, is produced: $PCl_5 + HOH \rightarrow POCl_3 + 2HCl$.

* This substance is a mixed anhydride (compare p. 434) of phosphoric acid and hydrogen chloride.

This interaction of phosphorus pentachloride and water is a perfectly general one, and takes place with most compounds containing hydroxyl. Thus, when alcohol (which differs from water in having ethyl C_2H_5, instead of hydrogen, combined with hydroxyl) is poured upon PCl_5, ethyl chloride, phosphoryl chloride, and hydrogen chloride are formed:

$$C_2H_5OH + PCl_5 \rightarrow C_2H_5Cl + POCl_3 + HCl.$$

The same action takes place with all carbon compounds containing hydroxyl, and is used as a means of showing the presence of this group in their structure.

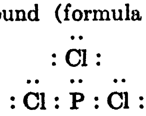
Phosphorus pentachloride, when heated under ordinary atmospheric pressure, *sublimes* (see p. 350) at 163°. When heated in a sealed tube under increased pressure it melts at 166°. In the saturated vapor at the subliming point, about 4 per cent of the molecules are dissociated into phosphorus trichloride and chlorine (p. 193): $PCl_5 \rightleftarrows PCl_3 + Cl_2$.

Phosphorus pentabromide, when vaporized, is also partly dissociated:

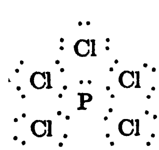
$$PBr_5 \rightleftarrows PBr_3 + Br_2.$$

Since the first two members of this equilibrium are colorless, while the bromine is brown, this action may be used to **illustrate** the effect upon a system, of **increasing the concentration of one of the interacting substances** (p. 270). Two tubes of equal volume and containing equal amounts of the pentabromide are prepared. A small amount of the tribromide is added to the second, and both are sealed up. When the tubes are now heated to the same temperature, the contents of the second will be less strongly colored by bromine in consequence of the greater activity in it of the reversing action.

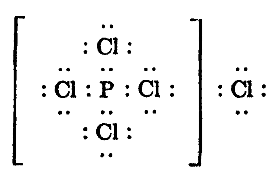
A difficulty arises in the representation of the electronic formula of phosphorus pentachloride, regarding which chemists are not yet in agreement. Phosphorus trichloride may be quite readily formulated as a co-valent compound in which each atom present has completed its outer electron shell of 8 (see I below). In the case of the pentachloride, however, we must either postulate the sharing of ten electrons by the central phosphorus atom, thus breaking the octet rule (formula II), or we must regard PCl_5 as a co-ordination compound (formula III).



I



II



III

But this last formula would demand that PCl_5 should be an electrolyte, like NH_4Cl, whereas pentachlorides are predominantly not salt-like in their behavior. As regards formula II, the same difficulty arises in the case of all heavier elements with co-ordination numbers greater than four (see p. 527), and the explanation must for the present be left in abeyance.

Oxides of Phosphorus. — The oxides of phosphorus are the trioxide P_2O_3, the pentoxide P_2O_5, and a tetroxide P_2O_4.

The **pentoxide** is a white powder formed when phosphorus is burned with a free supply of oxygen. It unites with water with great violence to form, finally, phosphoric acid H_3PO_4 (see below), and hence is known as **phosphoric anhydride.** In the laboratory this action is frequently utilized for drying gases (p. 138) and for removing water from combination (p. 387). The vapor density leads to the formula P_4O_{10}, use of which, however, would only complicate our equations in reactions in which the vapor state is not concerned.

The **trioxide** is obtained by burning phosphorus in a tube with a restricted supply of air. It is a white solid, melting at 22.5° and boiling at 173°. This oxide is the anhydride of phosphorous acid, but it unites exceedingly slowly with cold water to form this substance. When its vapor (the density of which corresponds to the formula P_4O_6) is heated to 440° it decomposes, giving the **tetroxide** P_2O_4 and red phosphorus.

Acids of Phosphorus. — There are six different acids of phosphorus. *Three* are phosphoric acids, representing the same stage of oxidation of phosphorus, but different degrees of hydration of the anhydride. The others show three different and lower states of oxidation (compare p. 391):

Orthophosphoric acid	H_3PO_4	Hypophosphoric acid	H_2PO_3
Pyrophosphoric acid	$H_4P_2O_7$	Phosphorous acid	H_3PO_3
Metaphosphoric acid	HPO_3	Hypophosphorous acid	H_3PO_2

When the same anhydride gives more than one acid, differing only in degree of hydration, the principle of nomenclature adopted is to call the more fully hydrated acid the *ortho*-acid, and the less fully hydrated acid the *meta*-acid. Thus, orthosilicic acid is H_4SiO_4 ($SiO_2,2H_2O$), and metasilicic acid is H_2SiO_3 (SiO_2,H_2O). The other prefixes employed in the above tabulation have already been explained (see p. 383).

The Phosphoric Acids. — The relation between the three different phosphoric acids may be seen by considering them as being formed from phosphorus pentoxide (the anhydride) and water. In

the majority of cases already considered this sort of action takes place in but one way. Thus, nitric acid is known in but one form, which is produced by the union of one molecule each of nitrogen pentoxide and water: $N_2O_5 + H_2O \rightarrow 2HNO_3$. Similarly, the chief sulphuric acid is the one formed from one molecule of sulphur trioxide and one molecule of water: $SO_3 + H_2O \rightarrow H_2SO_4$, although here we have also pyrosulphuric (fuming sulphuric) acid $H_2S_2O_7$, or $2SO_3,H_2O$. Periodic acid (p. 391) has a set of even more complexly related acids or salts.

Now, when phosphoric anhydride acts upon water we obtain a solution, which, on immediate evaporation, leaves a glassy solid, HPO_3, known as **metaphosphoric acid.** This is H_2O,P_2O_5. When, however, the solution is allowed to stand for some days, or is boiled with a little dilute nitric acid, the hydrogen-ion of which acts catalytically, the residue from evaporation is H_3PO_4, **orthophosphoric acid** (ordinarily called just **phosphoric acid**):

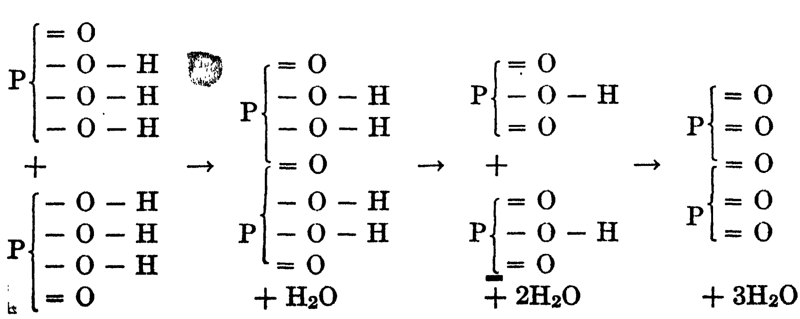
$$HPO_3 + H_2O \rightarrow H_3PO_4.$$

Conversely, when orthophosphoric acid (which is equivalent to $3H_2O,P_2O_5$) is kept at about 255° for a time, it slowly loses water, and $H_4P_2O_7$, **pyrophosphoric acid,** is obtained:

$$2H_3PO_4 \rightarrow H_2O + H_4P_2O_7.$$

This acid is $2H_2O,P_2O_5$. Further desiccation leaves metaphosphoric acid, which cannot be further resolved into phosphorus pentoxide and water. When dissolved in water, pyrophosphoric acid slowly resumes the water which it has lost and gives the ortho-acid again.

The relations of all these substances are more clearly seen in the graphic formulæ:



A most important fact to be noted is that the *addition or removal of water leaves the valence of the phosphorus unchanged.* The degree of oxidation of the phosphorus and its valence are *identical* in the three acids.

Pyrosulphuric acid and its salts when dissolved in water give sulphuric acid and acid sulphates, respectively. That is to say, the ion $S_2O_7^{=}$ is not capable of existence. But the very slow rate at which the less hydrated phosphoric acids change into the more hydrated ions shows that ions like PO_3^- and $P_2O_7^{==}$ may be comparatively stable. The behavior of solutions of the salts shows this even more clearly.

Orthophosphoric Acid H_3PO_4. — The impure, commercial acid is made by mixing selected, pulverized phosphate rock $Ca_3(PO_4)_2$ with sulphuric acid (sp. gr. 1.5) and heating with steam and stirring in a wooden vat:

$$Ca_3(PO_4)_2 + 3H_2SO_4 \leftrightarrows 2H_3PO_4 + 3CaSO_4 \downarrow .$$

The calcium sulphate is precipitated during the heating and the subsequent concentration of the filtrate.

Alternatively, in the method employed for the manufacture of phosphorus by heating phosphate rock with carbon and sand in the electric furnace (p. 542), the process is modified by introducing a current of air so as to oxidize the phosphorus, as it is formed, to the pentoxide P_2O_5. This distils over, and water is added to it to produce phosphoric acid. The chief use for the acid is in the fertilizer industry (see p. 613).

Pure orthophosphoric acid may be made by boiling red phosphorus with slightly diluted nitric acid and evaporating the water and excess of nitric acid. The product is a white, crystalline, deliquescent **hemihydrate,** $2H_3PO_4,H_2O$ (m.-p. 29.35°). Anhydrous orthophosphoric acid melts at 42.3°.

The acid is a typical transition acid (see table on p. 317), and is dissociated chiefly into the ions H^+ and $H_2PO_4^-$. The further dissociation of the latter ion into H^+ and $HPO_4^{=}$ takes place to only a very small extent. The ion $HPO_4^{=}$ also possesses only a very slight tendency to break up into H^+ and $PO_4^{\equiv}$. The concentration of these last-mentioned ions in an acid solution is therefore negligible.

$$H_3PO_4 \rightleftarrows H^+ + H_2PO_4^- \rightleftarrows H^+ + HPO_4^{=} \rightleftarrows H^+ + PO_4^{\equiv}.$$

Salts of Orthophosphoric Acid. — As a **tribasic acid,** it forms salts of three kinds, such as NaH_2PO_4, Na_2HPO_4, and Na_3PO_4. These are known respectively as **primary, secondary** and **tertiary**

sodium orthophosphate. The primary sodium phosphate is faintly acid in reaction (compare sodium bisulphite, p. 417). The secondary one is slightly alkaline, because of hydrolysis (compare acid sodium sulphide, p. 407). The tertiary phosphate is stable only in solid form (compare normal sodium sulphide, p. 406), and can be made by evaporating to dryness a mixture of the secondary phosphate and sodium hydroxide:

$$Na_2HPO_4 + NaOH \rightleftarrows Na_3PO_4 + H_2O \uparrow .$$

When the product is dissolved in water, this action is reversed (compare p. 409). Mixed phosphates are also known, particularly sodium-ammonium phosphate (**microcosmic salt**) $NaNH_4HPO_4,4H_2O$, and the insoluble magnesium-ammonium phosphate $MgNH_4PO_4$. Primary calcium phosphate (see p. 613), known in commerce as "super-phosphate," is used as a fertilizer.

The tertiary **phosphates** are unchanged by **heating.** The primary and secondary phosphates, however, retaining, as they do, some of the original hydrogen of the phosphoric acid, are capable of losing water, like phosphoric acid itself, when heated. The actions are slowly reversed when the products are dissolved in water:

$$NaH_2PO_4 \rightleftarrows NaPO_3 + H_2O \uparrow .$$
$$2Na_2HPO_4 \rightleftarrows Na_4P_2O_7 + H_2O \uparrow .$$

It will be seen that the **meta-** and **pyrophosphates of sodium** are formed by these actions; and this is indeed the simplest way of forming these substances, since the acids themselves are not permanent in solution, and are too feeble to lend themselves to exact neutralization. Ammonium salts of phosphoric acid lose ammonia, as well as water, when heated (see p. 514). Thus microcosmic salt first gives primary sodium phosphate:

$$NaNH_4HPO_4 \rightarrow NH_3 \uparrow + NaH_2PO_4 \rightarrow NaPO_3 + H_2O \uparrow,$$

and this in turn is converted into the metaphosphate by loss of water.

Pyrophosphoric Acid and Metaphosphoric Acid. — Pyrophosphoric acid $H_4P_2O_7$, although tetrabasic, gives only the normal salts, such as $Na_4P_2O_7$, and those in which one-half of the hydrogen has been displaced by a metal, such as $Na_2H_2P_2O_7$.

Metaphosphoric acid HPO_3 is the "glacial phosphoric acid" of commerce, and is usually sold in the form of transparent sticks. It is obtained by heating orthophosphoric acid, or by direct union of phosphorus pentoxide with a small amount of cold water. It passes into vapor at a high temperature, and its vapor density corresponds to the formula $(HPO_3)_2$.

Sodium metaphosphate $NaPO_3$, in the form of a small globule obtained by heating microcosmic salt on a platinum wire, is used in analysis. When minute traces of oxides of certain metals are placed upon such a globule, known as a **bead,** and heated in the Bunsen flame, the mass is colored in various tints according to the oxide used (**bead test**). This action may be understood when we consider that sodium metaphosphate takes up water to form primary sodium orthophosphate: $NaPO_3 + H_2O \rightarrow NaH_2PO_4$. In the same way, but at higher temperatures, it is able to take up oxides of elements other than hydrogen, giving mixed orthophosphates. Thus, with oxide of cobalt a part of the metaphosphate unites according to the equation:

$$NaPO_3 + CoO \rightarrow NaCoPO_4,$$

and the product gives a blue color to the bead.

Distinguishing Tests. — When a solution of **nitrate of silver** is added to a solution of orthophosphoric acid, or to any soluble orthophosphate, a yellow precipitate of silver orthophosphate Ag_3PO_4 is produced. This is a test for orthophosphates. With pyrophosphoric acid or any pyrophosphate the product is white $Ag_4P_2O_7$. With metaphosphoric acid a white precipitate, $AgPO_3$, is obtained also. Metaphosphoric acid coagulates a clear solution (colloidal suspension) of albumen (say, white of egg), while ortho- or pyrophosphoric acid has no visible effect upon it.

A test for orthophosphoric acid, or rather the ion $PO_4^{\equiv}$, consists in adding a drop of the solution containing this ion to a solution of ammonium molybdate (p. 883) in dilute nitric acid. A copious yellow precipitate of a complex ammonium phosphomolybdate appears on warming. In presence of excess of ammonia, the formation of the white insoluble ammonium-magnesium phosphate (p. 743) serves as a test also. Arsenic acid (p. 861) gives precipitates of appearance and composition similar to these two.

Phosphorous Acid H_3PO_3. — When added to cold water, phosphorus trioxide yields phosphorous acid very slowly. With hot water, violent and complex decompositions occur, and very little

phosphorous acid remains. This acid may be obtained much more easily by the action of water upon phosphorus trichloride (p. 231), tribromide or tri-iodide and evaporation of the solution:

$$PCl_3 + 3H_2O \rightarrow H_3PO_3 + 3HCl \uparrow .$$

Phosphorous acid is a powerful reducing agent, precipitating silver, for example, in the metallic form from solutions of its salts. When heated, it decomposes, giving the most stable acid of phosphorus (compare pp. 392, 417), namely metaphosphoric acid, and phosphine:

$$4H_3PO_3 \rightarrow 3HPO_3 + 3H_2O + PH_3.$$

Hypophosphorous Acid. — The potassium salt of this acid is obtained, as we have seen, when phosphorus is heated with potassium hydroxide solution (p. 546). It may be prepared in the free form by substituting barium hydroxide for potassium hydroxide:

$$3Ba(OH)_2 + 8P + 6H_2O \rightarrow 3Ba(H_2PO_2)_2 + 2PH_3 \uparrow .$$

By careful addition of dilute sulphuric acid to the resulting liquid, barium sulphate is precipitated. On evaporation of the water, the white crystalline acid H_3PO_2 is obtained. This substance is also a powerful reducing agent, tending, by the acquisition of oxygen, to pass into phosphoric acid.

The acid and its salts, when heated, give off water and phosphine, and leave phosphoric acid and phosphates, respectively. Thus, sodium hypophosphite gives phosphine and, finally, sodium pyrophosphate:

$$4NaH_2PO_2 \rightarrow 2PH_3 \uparrow + 2Na_2HPO_4 \rightarrow Na_4P_2O_7 + H_2O \uparrow .$$

Hypophosphoric Acid H_2PO_3. — When white phosphorus is heated under nitric acid, alone, orthophosphoric acid is formed. When, however, cupric nitrate (or silver nitrate; other nitrates are without effect) is added, copper is precipitated (as Cu_3P_2 or Cu). By neutralizing half of the resulting solution with sodium carbonate, and adding the other half, a copious precipitate of a hydrate of sodium hypophosphate $NaHPO_3,2H_2O$ appears. From this salt, other salts and the free acid can be prepared.

Sulphides of Phosphorus. — White phosphorus, when heated with sulphur, unites with explosive violence. By using red phosphorus the action can be controlled. By employing the proper

proportions, the **pentasulphide** P_2S_5 is secured. It is purified by distillation from a retort in which a current of carbon dioxide is maintained (see below). The distillate solidifies to a yellow, crystalline solid (m.-p. 290°, b.-p. 515°). Materials undergoing chemical change, which are to be kept at a constant, high temperature, are often placed in tubes suspended in the vapor of the pentasulphide. When a lower temperature is required, boiling sulphur (445°) is used.

Distillation in a stream of some inactive gas is a common means of distilling under reduced pressure (compare p. 367). The dilution of the vapor lowers its partial pressure, just as would evacuation. This plan has the advantage, however, of sweeping the vapor away from the heated region into the condenser, and so diminishing the amount of decomposition. In dealing with compounds of carbon, a current of steam (**steam distillation**) is often used for the above purposes. It enables us also to separate a slightly volatile substance from one which is almost involatile.

Phosphorus pentasulphide is hydrolyzed by cold water, and acts upon other substances containing hydroxyl when heated with them, the actions being similar to those of the pentachloride (p. 549):

$$P_2S_5 + 8H_2O \rightarrow 2H_3PO_4 + 5H_2S.$$

Other sulphides, P_4S_3 (used in making matches, p. 545), and P_4S_7, may be prepared by using the constituents in the proportions represented by these formulæ.

Comparison of Phosphorus with Nitrogen and with Sulphur. — Although phosphorus and nitrogen are regarded as belonging to one family, the differences between them are more conspicuous than the resemblances. The latter are confined almost wholly to matters concerned with valence. The contrasts between phosphine and ammonia (p. 547) and between the halides of the two elements (pp. 517, 548) have been noted already. The pentoxide of nitrogen decomposes spontaneously; that of phosphorus is one of the most stable of compounds. Nitric acid is very active, both as acid and oxidizing agent; the phosphoric acids are quite the reverse.

On the other hand, the resemblance of phosphorus to sulphur is marked. Both are solids, existing in several forms. Both yield stable compounds with oxygen and chlorine. The hydrogen compounds interact with salts to give phosphides of metals and sulphides of metals, respectively. Against these must be set the

facts, that hydrogen sulphide does not unite with the hydrogen halides at all while phosphine gives the phosphonium halides, and that phosphoric acid is hard to reduce while sulphuric acid is reduced with comparative ease.

Exercises. — What are the valences of the non-metals in: $H_2S_2O_7$, $H_2Cr_2O_7$, $KMnO_4$, KH_2PO_2, H_3PO_4, NaH_2PO_3, Na_2PO_3? Name these substances.

2. Is it oxidation or reduction, or neither, when we make, (*a*) N_2O_4 from HNO_3, (*b*) SO_2 from H_2SO_3, (*c*) HPO_3 from H_3PO_3, (*d*) $H_2S_2O_7$ from H_2SO_4, (*e*) Na_2SO_4 from $NaHSO_3$?

3. Why would a mixture of potassium dichromate and hydrochloric acid (p. 405) be less suitable than nitric acid as an oxidizing agent for making phosphoric acid from red phosphorus?

4. Why is not the tertiary phosphate of sodium (p. 553) decomposed by heating? What tertiary phosphates would be decomposed by this means?

5. Formulate the hydrolysis of the secondary and tertiary sodium orthophosphates as was done for sodium sulphide (pp. 406–7).

6. How should you prepare $Ca_2P_2O_7$ and $Ca(PO_3)_2$, both insoluble?

7. What product should you confidently expect to find (p. 555) after heating, (*a*) sodium phosphite, Na_2HPO_3, (*b*) potassium hypophosphite (p. 546)? Make the equations.

8. Compare the elements chlorine and phosphorus after the manner of the comparisons in the last paragraph of this chapter.

9. What is the percentage composition of calcium phosphate $Ca_3(PO_4)_2$? What weight of phosphorus can be obtained from 200 g. of the substance? Write the equation.

10. What volume of phosphine at 20° and 750 mm. will be obtained by heating 10 g. of white phosphorus with excess KOH?

11. What volume of phosphine at 20° and 750 mm. will be obtained by the action of excess water on 10 g. of calcium phosphide?

12. Explain why the yield of phosphine in Exercise 10 is less than that in Exercise 11.

13. Excess water is added to 10 g. of phosphorus pentachloride, care being taken to let none of the reaction products escape. The solution is made up to 1 liter. What is its normality as an acid?

14. What is the percentage composition of micromosmic salt $NaNH_4HPO_4$, $4H_2O$?

15. Starting with tertiary sodium orthophosphate Na_3PO_4, devise a method of preparing each of the following substances: (*a*) sodium metaphosphate, (*b*) sodium pyrophosphate, (*c*) microcosmic salt.

16. Write the electronic formulæ of phosphorus pentoxide, metaphosphoric acid, pyrophosphoric acid and orthophosphoric acid.

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CHAPTER XXXII

CARBON AND THE OXIDES OF CARBON

The majority of the substances composing, or produced by, living organisms, such as fat, starch, and sugar, are compounds of carbon. Hence the chemistry of these compounds is known as **organic chemistry.** It was at first supposed that the artificial production of such compounds, *e.g.*, without the intervention of life, was impossible. But many natural organic products have now been made from simpler ones or from the elements, and the preparation of the others is delayed only in consequence of difficulties caused by their instability and complexity. On the other hand, thousands of compounds unknown to animal or vegetable life, including many valuable drugs and dyes, have now been added to the catalogue of organic chemical compounds by synthesis in the laboratory (see Chapter XXXVIII. Hundreds of thousands of different compounds containing carbon are known, and thousands more are added every year.

The elements entering into carbon compounds are chiefly hydrogen and oxygen. After these, nitrogen, phosphorus, the halogens and sulphur may be named.

Carbon C

The Chemical Relations of the Element. — The elements of the carbon family are carbon, silicon, germanium, tin, and lead (see Periodic system). Of these the first two are entirely non-metallic, while the others are metallic elements showing more or less strong resemblances to the non-metals. All these elements are quadrivalent as regards the maximum valence which they exhibit. With the exception of silicon, however, they all form many compounds in which they are bivalent.

Occurrence. — Large quantities of carbon are found in the free condition in nature. The **diamond** is the purest natural carbon. **Graphite,** or plumbago, which is the next purest, is found in limited amounts, and is a valuable mineral. **Coal** occurs in numerous forms containing greatly varying proportions of free carbon. Small quantities of the free element have been found in meteorites.

In combination, carbon is found in **marsh-gas,** or **methane** CH_4, which is the chief component of natural gas. The numerous compounds found in plants and animals have already been mentioned. The **mineral oils** consist almost entirely of mixtures of various compounds of carbon and hydrogen (hydrocarbons). Whole geological formations are composed of *carbonates of common metals,* particularly **calcium carbonate** or **limestone.**

Diamond. — This allotropic modification of carbon is distinguished by its natural crystalline form, which often resembles the octahedron (Fig. 18, p. 60). The ultimate structure of the diamond crystal is represented in Fig. 38 (p. 70). Its specific gravity is 3.5. For ornamental purposes the diamond is "cut" by grinding new faces so as to give artificial forms called "brilliants" (Fig. 161) and "rosettes." These forms are given to the stone, in order

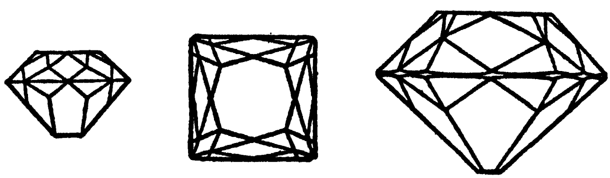


FIG. 161. Cut Diamonds.

that the maximum reflection of light from its interior may be produced. It is the hardest of familiar substances, and can be scratched or polished only by rubbing with diamond powder. The colorless stones and those with special tints are very valuable. The black ("carbonado") and badly colored specimens are less valuable and are used for grinding, for glass-cutting, and on the points of drills.

Diamonds are found chiefly in South Africa and Brazil. They are separated from the rock by weathering and washing. They are sold by the carat (1 international carat = 200 mg.) and the value increases with the size. The largest known specimen, the Cullinan, weighed 3032 carats before being cut. Small synthetic diamonds are obtained when molten iron containing dissolved carbon is suddenly chilled. If the fused mass is allowed to cool gradually, however, the carbon separates out in the form of graphite.

Graphite. — Graphite (Greek, *I write*) is found in nature in Siberia, Cumberland, Brazil, Ceylon and elsewhere. It forms dark gray or black hexagonal tablets, and, when pulverized, it gives slippery scales of microscopic size. Its crystal lattice structure is indicated in Fig. 162. Unlike the diamond, it is quite soft, has a specific gravity of 2.3, and conducts the electric current. Natural

graphite is usually mixed with foreign matter, and even the purest specimen leaves, when burned, from 2 to 5 per cent of ash. It is called also **plumbago** or **black lead.**

Graphite, molded into blocks, is sawn into rods for the cores of "lead" pencils. Clay is added in varying proportions to give different degrees of hardness. Because of its infusibility, it is used

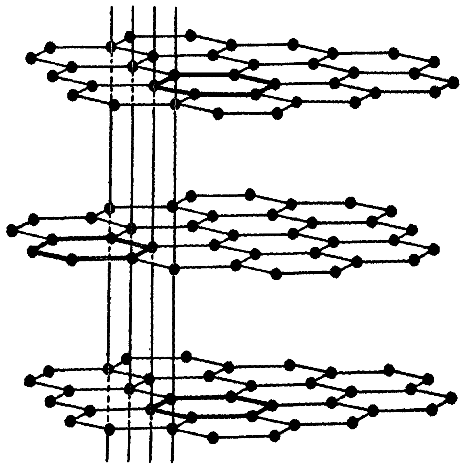


FIG. 162. Crystal Lattice Structure of Graphite.

to make crucibles. Smeared on a plaster cast (non-conductor), it gives a conducting surface on which metals (copper or silver) can be deposited by electrolysis. A thin layer, used as stove-polish, protects the iron from rusting. In electrochemical industries it is used for electrodes at which chlorine is to be liberated; all other conductors either interact chemically with this element and are destroyed, or are too expensive for large-scale use. It is employed also as a lubricant, when wooden beams slide upon one another.

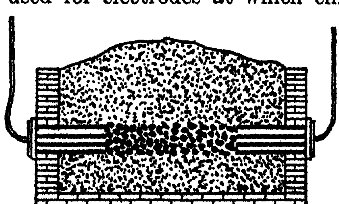


FIG. 163. Manufacture of Graphite.

Large amounts of pure graphite are now manufactured by heating coke with some pitch and a little sand or ferric oxide (Acheson's process). The mixture (3 to 3½ tons) is piled (Fig. 163) between electrodes connected with a dynamo, and, on account of

its high resistance, becomes strongly heated. The operation is complete in from 24 to 30 hours.

Other Forms of Carbon. — The apparently amorphous varieties of carbon are numerous. They include **wood-charcoal, lampblack, animal charcoal, coal** (*e.g.*, bituminous coal and anthracite) and **coke.** All of these substances will come up for discussion in later chapters. None of them, it may be noted here, is composed of pure carbon, other elements being present, mostly in combination with carbon, in very variable amounts.

Examination of *"amorphous"* charcoal by X-ray methods indicates that it possesses a hexagonal lattice structure *identical* with that of graphite. Charcoal is not to be regarded, therefore, as a supercooled liquid (see p. 62) like glass. It consists of tiny fragments of graphite. The amorphous appearance is due to the extreme minuteness of the crystals, which are interspersed, with attendant impurities, through a highly porous mass.

Chemical Properties of Carbon. — The most common uses of carbon depend upon its great tendency to **unite with oxygen,** forming carbon dioxide CO_2. With a limited supply of oxygen, carbon monoxide CO (see p. 569) is produced. Aside from the direct employment of these reactions for the sake of the heat which is liberated (see p. 255), they are used also in the **reduction of ores** of iron, copper, zinc, and many other metals. When, for example, finely powdered cupric oxide and carbon are heated, copper is obtained. The gas given off is either carbon dioxide, or a mixture of this with carbon monoxide, according to the proportion of carbon and the temperature used:

$$CuO + C \rightarrow Cu + CO$$
$$2CuO + C \rightarrow 2Cu + CO_2.$$

At the high temperatures produced in the electric furnace, carbon **unites** with many **metals** and some **non-metals.** Thus, when dissolved in molten iron, it forms **iron carbide** Fe_3C. Other examples will be taken up in succeeding sections.

The **union with hydrogen** is ordinarily too slow to be observed. But when the carbon is mixed with pulverized nickel (contact agent), and hydrogen is passed over the mixture at 300°, methane CH_4 is formed (97 per cent). The action is reversible and exothermal, and is therefore, at higher temperatures, less complete (see p. 284), at 850° reaching only 1.6 per cent. On the other hand, an electric arc, between carbon poles in an atmosphere of hydrogen, gives traces of acetylene C_2H_2, this action being endo-

thermal. The other compounds of carbon and hydrogen are all obtained by indirect reactions.

Carbon Disulphide CS_2. — This compound is made by direct union of sulphur vapor and glowing charcoal. An electric furnace like that in Fig. 159 (p. 542) is employed. The substance comes off as a vapor and is condensed.

Carbon disulphide is a colorless, highly refracting liquid (b.-p. 46°). Traces of other compounds gives the commercial article a disagreeable smell. It burns in air, forming carbon dioxide and sulphur dioxide. It is an important solvent for sulphur and caoutchouc (rubber). Large quantities are employed also in the destruction of prairie dogs and ants, and for freeing grain elevators of rats and mice.

Carbon Tetrachloride CCl_4. — This compound is manufactured by leading dry chlorine into carbon disulphide containing a little iodine (as catalyst) in solution:

$$CS_2 + 3Cl_2 \rightarrow CCl_4 + S_2Cl_2.$$

On distilling the resulting mixture, the carbon tetrachloride CCl_4 (b.-p. 77°) passes off and is condensed, while the sulphur monochloride S_2Cl_2 (b.-p. 136°) remains.

Carbon tetrachloride is a colorless liquid. It dissolves fats and tars and other organic compounds, and has the advantage over benzine and gasoline of being non-inflammable. It is therefore used in taking the grease out of wool, linen cloth, oil-bearing seeds, and bones. Many liquids sold for dry-cleaning and removing stains from clothing, gloves, etc., consist of carbon tetrachloride diluted with a cheaper material, such as benzine (p. 578). Although the proportion of such material originally added may be insufficient to render the mixture inflammable or explosive, the risk exists that evaporation of the more volatile carbon tetrachloride may eventually bring the composition of the residue into the dangerous region. Products containing no benzine are therefore to be preferred.

"Pyrene" fire extinguishers contain, mainly, carbon tetrachloride. When this is squirted upon a fire, the temperature of the burning material is lowered, because heat is consumed in vaporizing the liquid and, at the same time, the vapor displaces the air and stops the combustion.

Carbides and the Electric Furnace. — Chemical actions which proceed only at very high temperatures are most economically car-

ried out by using electricity as the source of heat. In such cases the electricity has no electrolytic or other chemical action. There are several types of electric furnaces. In the making of graphite (p. 560), which illustrates a *resistance furnace,* the poor conductivity of the carbon between the electrodes furnishes the occasion for the rise in temperature. Of the same type is the furnace used for making **carborundum** (SiC, silicon carbide), manufactured in large quantities at Niagara Falls (Acheson's process). The coke and sand (silicon dioxide SiO_2) are piled between the terminals, and the resistance of the former causes the production of the heat, as in Fig. 163, p. 560:

$$3C + SiO_2 \rightarrow SiC + 2CO\uparrow .$$

Here the carbon reduces the oxide, and combines with the element (Si) as well. The product (SiC) is exceedingly hard, and, after pulverization and mixing with other materials, is molded into grinding wheels.

In an *arc furnace* the gases between the terminals furnish the resistance, and the *arc* (a discharge carried by the badly conducting gas) furnishes the heat. This type of furnace is employed in various "arc processes" for the fixation of atmospheric nitrogen (p. 530).

The arc is also of assistance in the manufacture of **calcium carbide** (CaC_2), which involves the heating of a mixture of lime and coke to a very high temperature (estimated at 3000°). The reaction is carried out in large graphite crucibles which form the negative electrodes. The positive electrodes consist of large blocks of graphite, which are gradually consumed in the passing of the arc:

$$CaO + 3C \rightarrow CO + CaC_2.$$

Cold water acts vigorously upon calcium carbide, giving **acetylene** gas C_2H_2 (see p. 585) and calcium hydroxide (slaked lime):

$$CaC_2 + 2H_2O \rightarrow Ca(OH)_2 + C_2H_2\uparrow .$$

The Oxides of Carbon. — Four oxides of carbon are known, of which two, namely the dioxide CO_2 and the monoxide CO, are familiar. Carbon suboxide C_3O_2 and mellitic anhydride $C_{12}O_9$ are best classed as organic compounds. Two other oxides, C_5O_5 and

C_6O_6, are known only in hydrated forms, namely leuconic acid and triquinoyl, respectively.

Carbon Dioxide and Carbonic Acid

Occurrence. — Carbon dioxide is present in the atmosphere, and issues from the ground in large quantities in certain neighborhoods, as, for example, in the so-called Valley of Death in Java, and in the Grotta del Cane near Naples. Effervescent mineral waters, such as those of Vichy and of the Geyser Spring at Saratoga, contain it in solution, and their effervescence is caused by the escape of the gas when the pressure is reduced.

Modes of Formation. — 1. Carbon dioxide is produced by combustion of carbon with an excess of oxygen: $C + O_2 \rightarrow CO_2$. The combustion of all compounds of carbon, as well as the slow oxidation in the tissues of plants and animals, yields the same product. The product from burning carbon is naturally mixed with at least four times its volume of atmospheric nitrogen. To secure carbon dioxide for commercial purposes from this source, the gas is led under pressure into a solution of potassium carbonate, which absorbs the carbon dioxide (see p. 566). When the pressure is reduced by a pump, the action is reversed, and the gas escapes in pure form. The same solution, with occasional purification, can be used an indefinite number of times.

2. It was Joseph Black, Professor of Chemistry in the University of Edinburgh, who first (1757) recognized the gas as a distinct substance. He observed its formation when marble or chalk was heated:

$$CaCO_3 \rightleftarrows CaO + CO_2,$$

and named the gas "fixed air" from the fact that it was contained in these solids. The above action has been used for centuries in making quicklime (calcium oxide). All common carbonates, excepting those of potassium and sodium, decompose when heated, the oxide of the metal or the metal itself remaining.

3. Black found that the gas was also produced when acids acted upon carbonates, and this is the method employed in the laboratory:

$$CaCO_3 + 2HCl \rightleftarrows CaCl_2 + H_2CO_3$$
$$H_2CO_3 \rightleftarrows H_2O + CO_2 \uparrow.$$

The apparatus shown in Fig. 67 (p. 133) is used.

4. Carbon dioxide is formed in decay (p. 97) and, as Black likewise discovered, in fermentation (see p. 618). Large quantities are collected for industrial use from the vats in which beer is brewed.

Physical Properties. — Carbon dioxide is a colorless, odorless gas. It is heavier than air (p. 251). Its critical temperature is 31.35° (p. 124). The solid melts at — 56°, having a vapor pressure of 5.3 atmospheres. The sp. gr. of the liquid at 0° is 0.95. At 0° its vapor tension is 35.4 atmospheres and at 20°, 59 atmospheres. It must be preserved, therefore, in very strong cylinders of mild steel. Large quantities of it are sold in such cylinders, and used in making aërated waters. When the liquid is allowed to flow out into an open vessel or, still better, into a cloth bag (non-conductor of heat), it cools itself by its own evaporation and forms a white, snowlike mass. Solid carbon dioxide evaporates under atmospheric pressure at — 79°, without melting.

The solid (**Dry Ice**) has recently come into commercial use as a refrigerant. It is used in the laboratory as a cooling agent, being often mixed with ether or alcohol to give closer contact with the vessel containing the substance to be cooled. Mercury (m.-p. — 40°) is easily frozen by the mixture.

The great contrast in the speeds of a chemical change at two temperatures (compare p. 99) may be illustrated by putting a minute piece of sodium in some 30 per cent hydrochloric acid which has been cooled in the above mixture. Hardly any interaction can be observed. But if the temperature of the acid is allowed to rise, the action becomes more and more rapid, and ends by being explosively violent.

Carbon dioxide gas dissolves in its own volume of water (760 mm. and 15°). Up to four or five atmospheres Henry's law (p. 219) describes its solubility accurately. An aqueous solution, under a pressure of 3–4 atmospheres, is familiarly known as **soda water,** or carbonated water.

Chemical Properties. — Carbon dioxide is a stable compound. At 2000° and 760 mm., the dissociation reaches 1.8 per cent, or about the same as that of water: $2CO_2 \rightleftharpoons 2CO + O_2$.

The more active metals, like magnesium, burn brilliantly when ignited in a hollow lump of solid carbon dioxide, producing the

oxide and free carbon. Less active metals, such as zinc and iron, when heated in a stream of the gas, give an oxide of the metal and carbon monoxide.

Carbon dioxide unites directly with many oxides, particularly those of the more active metals, such as the oxides of potassium, sodium, calcium, etc., giving the carbonates. Hence the decomposition of calcium carbonate by heating (p. 564) is a reversible action, which proceeds in the opposite direction when a sufficient pressure of carbon dioxide is used (see p. 724).

Carbon dioxide, when dissolved in water, forms an unstable acid:

$$H_2O + CO_2 \rightleftarrows H_2CO_3, \quad \text{or} \quad \begin{matrix}H\diagdown\\ H\diagup\end{matrix}\!O + C\!\begin{matrix}/\!\!/O\\ \backslash\!\!\backslash O\end{matrix} \quad \rightarrow \quad \begin{matrix}H-O\diagdown\\ H-O\diagup\end{matrix}\!C = O.$$

The name carbonic acid is frequently, though improperly, given to the anhydride CO_2, which has no acid properties.

Chemical Properties of Carbonic Acid H_2CO_3. — The solution of carbon dioxide in water exhibits the properties of a *very* weak acid. It conducts electricity, although not well. It turns litmus faintly red. The ionization takes place chiefly according to the equation:

$$H_2CO_3 \rightleftarrows H^+ + HCO_3^-.$$

The further ionization of HCO_3^- into H^+ and $CO_3^=$ is exceedingly minute.

Carbonates and Bicarbonates. — When excess of an aqueous solution of carbonic acid is mixed with a solution of a base like sodium hydroxide, or, as the operation is more usually performed, when carbon dioxide is passed into a solution of the alkali, until the liquid is saturated, water is formed and the acid carbonate (**bicarbonate**) of sodium remains dissolved:

$$H_2CO_3 + NaOH \leftrightarrows H_2O + NaHCO_3.$$

Although the bicarbonate is technically an acid salt, its solution is very weakly alkaline (compare sodium hydrosulphide, p. 406).

By addition of an equivalent of sodium hydroxide, the normal carbonate is obtained:

$$NaOH + NaHCO_3 \rightleftarrows H_2O + Na_2CO_3.$$

This solution, like that of all normal salts of a strong base and a feeble acid (see p. 408), is decidedly alkaline in reaction.

The **normal carbonates,** with the exception of those of potassium, sodium, and ammonium, are insoluble in water, and may be obtained by precipitation when the proper ions are employed. For example:

$$BaCl_2 + Na_2CO_3 \leftrightarrows BaCO_3 \downarrow + 2NaCl.$$

The aqueous solution of carbon dioxide interacts with solutions of barium and calcium hydroxides in a similar manner:

$$Ca(OH)_2 + H_2CO_3 \leftrightarrows CaCO_3 \downarrow + 2H_2O.$$

These precipitations are used as **tests** for carbon dioxide or carbonates (see p. 458).

Excess of carbon dioxide converts calcium carbonate into the more soluble bicarbonate, and hence considerable quantities of "lime" are frequently held in solution by natural waters (see hardness, p. 729) which contain carbon dioxide in solution:

$$H_2CO_3 + CaCO_3 \rightleftarrows Ca(HCO_3)_2.$$

A considerable excess of carbon dioxide is required to convert the whole of the carbonate into the soluble bicarbonate, since the action is markedly reversible. In the same fashion, the carbonates of iron $FeCO_3$ (chalybeate water), magnesium, and zinc are dissolved as bicarbonates in water containing free carbonic acid. In fact, the solution, transportation, and deposition of all these carbonates take place in nature on a large scale by the alternate progress and reversal of this action (see p. 724).

Uses of Carbon Dioxide.—In addition to the commercial uses already mentioned, carbon dioxide is employed in immense quantities in the manufacture of sodium bicarbonate $NaHCO_3$ (baking soda), of sodium carbonate $Na_2CO_3,10H_2O$ (washing soda), and of white lead, a basic carbonate of lead $Pb_3(OH)_2(CO_3)_2$.

Since carbon dioxide is already fully oxidized, it does not burn, and since it is very stable, ordinary combustibles will not burn in it. A small percentage of it will destroy the power of air to support combustion. For this reason, portable **fire extinguishers** (Fig. 164) contain a dilute solution of sodium bicarbonate and a bottle of sulphuric acid. When the tank is inverted, the acid flows into the solution:

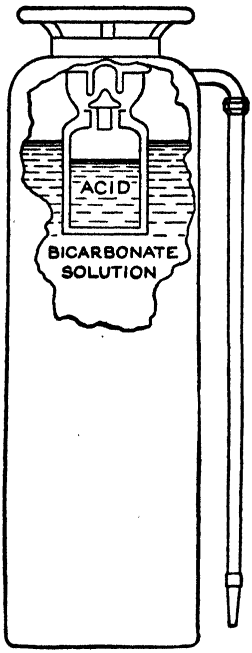


FIG. 164. Portable Fire Extinguisher.

$$2NaHCO_3 + H_2SO_4 \rightleftarrows Na_2SO_4 + 2H_2CO_3$$
$$H_2CO_3 \rightleftarrows H_2O + CO_2 \uparrow .$$

The liquid forced out through the nozzle by the pressure of the released gas is more effective in extinguishing a fire than an equal amount of water, because the carbon dioxide it carries mixes with the surrounding air.

The most wonderful chemical change which carbon dioxide undergoes, however, is the action in nature by which *plants use it as food.* This important action is discussed in detail in a later chapter (p. 598).

CARBON MONOXIDE CO

Preparation. — In the laboratory, carbon monoxide may be obtained by heating oxalic acid $(COOH)_2$, a solid, white, crystalline substance (p. 583), in a flask with concentrated sulphuric acid. The latter is here employed simply as a dehydrating agent (p. 427):

$$H_2C_2O_4 \rightarrow CO_2 + CO + H_2O.$$

To obtain pure carbon monoxide from this mixture, it is necessary to remove the carbon dioxide, by passing the gas through a solution of potassium hydroxide contained in a wash bottle. By using formic acid H.COOH (p. 583), or sodium formate, with sulphuric acid, the presence of the carbon dioxide is avoided: $H.COOH \rightarrow CO + H_2O$.

We commonly observe the blue flame of burning carbon monoxide playing on the surface of a coal fire (Fig. 165). The gas is

produced by the passage of the carbon dioxide, which is first formed, through the upper layers of heated coal: $CO_2 + C \rightarrow 2CO$. A similar reduction of carbon dioxide is produced when the gas is led over a metal, such as zinc, and heat is applied: $CO_2 + Zn \rightarrow ZnO + CO$.

Producer Gas and Water Gas. — When *a limited supply* of air is led through burning coke, the mixture of carbon monoxide (40 per cent) with nitrogen (60 per cent) obtained is called **producer**

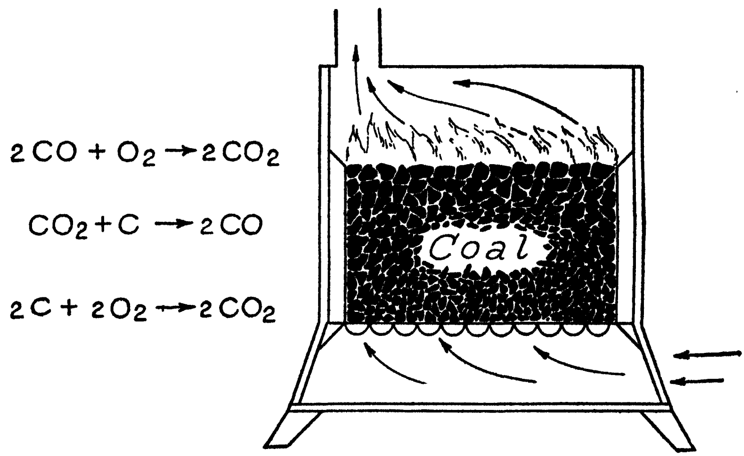


FIG. 165. Reactions in a Coal Fire.

gas. It is combustible, and is used in industrial establishments for heating and to drive gas engines for power.

Commercially, large amounts of carbon monoxide mixed with hydrogen (**water gas**) are manufactured by *blowing steam over white hot coke* or anthracite:

$$C + H_2O \rightarrow CO + H_2 - 29{,}100 \text{ calories.}$$

The coke is first set on fire in a brick-lined cylindrical structure and brought to vigorous combustion by blowing in air for ten minutes. Then steam is substituted for the air.

The interaction, as the equation shows, takes place with absorption of heat. Hence, at the end of a few minutes, the coke becomes too cool. It is then necessary to turn the steam off and to turn the air on again, and so on alternately. The mixture of car-

bon monoxide (40 to 50 per cent) and hydrogen (45 to 50 per cent), containing also some carbon dioxide (4 to 7 per cent), nitrogen (4 to 5 per cent), and oxygen (1 per cent), is known as **water gas.** It is almost wholly combustible, burning with a blue flame, and is used as a source of heat and, by driving internal combustion engines, to furnish power. It is used also in manufacturing illuminating gas (see p. 591).

If both air and steam are driven *together* over the burning coke, the air enables the coke to burn continuously, and a fuel gas which is a cross between producer gas and water gas is obtained. A gas of this type, with its proportions so adjusted as to give (after elimination of CO as described below) a mixture of N_2 and H_2 in the volume ratio of 1 : 3, is frequently employed in the Haber process (p. 508).

Fuel gases are employed on a large scale in steel works and other industrial plants. They give a uniform and easily regulated heat, they leave no ash, and their use involves no labor for stoking.

Industrial Hydrogen from Water Gas. — Hydrogen is required in large quantities in chemical industry for the manufacture of *ammonia* (p. 508) and for *hydrogenating oils* (p. 634). It is essential that this hydrogen should be carefully purified from traces of other gases, such as carbon monoxide and sulphuretted hydrogen, which act as poisons on the catalysts employed in the above processes. The cheapest source of industrial hydrogen is *water gas,* and much work has been done to devise a method for eliminating the undesirable carbon monoxide from this.

When a mixture of water gas (substantially $H_2 + CO$) and superheated steam is passed over a suitable catalyst, such as iron oxide, a reaction occurs as follows:

$$CO + H_2O \rightleftarrows CO_2 + H_2 + 9800 \text{ calories.}$$

The reaction being reversible, and exothermic in the forward direction, its equilibrium point is displaced towards the left, favoring the backward reacaction, as the temperature is raised. It is therefore desirable to work the process at as low a temperature as possible. With iron oxide alone as a catalyst, however, the interaction between the gases becomes too slow to be effective at temperatures much below 600°. The addition of small quantities of other oxides, such as nickel oxide and chromium oxide, has been found to increase the activity of the catalyst very considerably. Substances which act in this manner (catalyzing a catalyst, so to speak) are termed **promoters.**

In actual practice the reaction, carried out at 450°–500°, gives a mixture of gases containing only about 2 per cent residual CO. Excess of steam is employed to drive the equilibrium as far as possible towards the right, but the excess of hydrogen present in the original water gas favors, of course, the opposite reaction (compare p. 270). It should be noted that nearly *twice* as much hydrogen as was contained in this water gas is obtained by the process, the second half being derived from the decomposition of the steam.

The bulk of the carbon dioxide present in the final mixture (approximately 30 per cent by volume) is removed by washing the gas with water under pressure. The last traces of carbon dioxide are absorbed by means of lime or caustic soda. The removal of the 2 per cent residual CO presents difficulties. Absorption of CO by hot caustic soda solutions and by ammoniacal solutions of cuprous salts has been employed. The most efficient method, however, consists of **preferential combustion** of CO to CO_2 with the requisite quantity of air or oxygen in the presence of a second oxide catalyst. If due precautions are taken, CO burns almost quantitatively to CO_2 without any H_2 present burning to H_2O. The small amount of CO_2 formed is then removed as already described.

Physical Properties of Carbon Monoxide. — Carbon monoxide is a *colorless, odorless,* and *tasteless* gas. It is a *little lighter* than air (mol. wt. 28), and is very slightly *soluble* in water. It is difficult to *liquefy.* Its boiling-point, when liquid, is —190°, close to that of liquid air.

Chemical Properties. — All the chemical properties of carbon monoxide are referable to the fact that in it the element carbon appears to be bivalent: $C = O$. The compound is in fact **unsaturated,** and combines with oxygen, chlorine, and other substances directly. Thus, when set on fire, the gas *burns* in air or oxygen with a blue flame. Carbon dioxide is formed, and the presence of the latter may be shown with lime-water (p. 567):

$$2CO + O_2 \rightarrow 2CO_2.$$

On account of this tendency to combine with oxygen, carbon monoxide *reduces* the oxides of the less active metals, such as those of iron and of the metals below iron in the order of activity. Commercially, the ores of iron are reduced by this gas (essentially producer gas) in the blast furnace (p. 895).

In sunlight carbon monoxide unites directly with chlorine to form the poisonous gas **carbonyl chloride** (phosgene) $COCl_2$. It unites with nickel and iron to form nickel carbonyl and iron carbonyl (see p. 909), respectively.

Carbon monoxide is very toxic, 1 volume in 100,000 volumes of air producing symptoms of poisoning, while one volume in 750 to 800 volumes produces death in about thirty minutes. The gas combines with the hæmoglobin of the blood corpuscles, forming a stable compound, and thus preventing the absorption of oxygen by the blood (p. 97). This gas is the chief poisonous substance in illuminating gas. The poisonous effect of tobacco smoke, particularly

when inhaled, is also due mainly to the carbon monoxide produced by the necessarily incomplete combustion.

Combustions or explosions in confined spaces (such as in an automobile engine, in a mine-shaft, or in the interior of a warship during an engagement) have caused many deaths through CO poisoning. Gas masks for use in rescue work in such cases are fitted with canisters containing a mixture of metallic oxides, such as MnO_2, CuO, Co_2O_3, and Ag_2O (**hopcalite**). A mixture of this kind acts catalytically, any carbon monoxide passing into the canister being oxidized to carbon dioxide by the oxygen of the air.

Carbonyl Chloride and Urea

Carbonyl Chloride $COCl_2$.—This substance is also named **phosgene** (Greek *φῶς*, light; *γεννᾶν*, to produce), on account of its formation by the catalytic influence of sunlight (p. 245). On a commercial scale it is obtained by passing the mixed carbon monoxide and chlorine over animal charcoal (contact agent). It is a liquid which boils at 8°, possesses a suffocating odor and highly toxic properties (see p. 655), and is very soluble in benzene and some other hydrocarbons. When brought into contact with water it is hydrolyzed, forming carbonic acid and hydrochloric acid:

$$COCl_2 + 2H_2O \rightarrow H_2CO_3 + 2HCl.$$

Urea.—When ammonia and carbonyl chloride are mixed in the proper proportions, in an inert solvent such as toluene (p. 587), urea, a most interesting chemical substance, is produced:

$$O = C\begin{matrix} \diagup Cl \\ \diagdown Cl \end{matrix} + \begin{matrix} H - NH_2 \\ H - NH_2 \end{matrix} \rightarrow O = C\begin{matrix} \diagup NH_2 \\ \diagdown NH_2 \end{matrix} + 2HCl.$$

Excess of ammonia has to be used to combine with the hydrogen chloride thus set free, so that the final equation is:

$$COCl_2 + 4NH_3 \rightarrow CO(NH_2)_2 + 2NH_4Cl.$$

The urea, a white, crystalline solid, is soluble in alcohol, while ammonium chloride is not, so that the former may be washed out by means of this solvent and recovered by evaporation. A little reflection will show that, using the above action as the final stage, urea can be built up (**synthesized**) from the simple substances composing it.

Urea was known long before any method for its synthesis had been discovered. It is the chief product of the decomposition of compounds of nitrogen in the animal body, and is found in the liquid excrements of animals. It was regarded as a typical organic substance, in the old sense of the word (p. 558). In 1828, Wöhler succeeded in preparing it artificially (see below). This was the first synthesis by a chemist of a true "organic" substance, and its preparation proved to be the precursor of many discoveries of a similar nature. From a later year, about 1840, we may date the transition of organic chemistry, a science in which the mystery of life was supposed to be supreme, into the chemistry of the compounds of carbon, which is a branch of inorganic chemistry.

Wöhler used ammonium cyanate (p. 575), a substance in whose preparation we are independent of all products of life processes. When ammonium cyanate, or a mixture of any ammonium salt with potassium cyanate in solution in water, is warmed for some time, an intramolecular change (see p. 232) takes place, and long prisms of urea are deposited as the liquid cools:

$$NH_4.NCO \rightleftarrows CO(NH_2)_2.$$

Since the action is reversible, about four or five per cent of the ammonium cyanate remains unchanged.

The two substances just mentioned are entirely different in chemical properties. Ammonium cyanate is a highly ionized salt, while urea is not a salt at all, but a substance like ammonia which unites with acids to form salts. Materials which, like these, have the same composition and the same numbers of units in their molecules, and yet possess different properties, are spoken of in chemistry as **isomers.** The formulæ we have employed attempt to explain the differences in their properties by suggesting a difference in their molecular structure (compare p. 369).

Assisted by the catalytic action of certain ferments, urea, when dissolved in water, can take up two molecules of the solvent to form ammonium carbonate:

$$CO(NH_2)_2 + 2H_2O \rightarrow (NH_4)_2CO_3 \rightleftarrows 2NH_3 + H_2O + CO_2.$$

Ammonium carbonate (p. 709) is an unstable compound, and in turn gives off ammonia and carbon dioxide. To this action is due in part the strong odor of ammonia arising from the decomposition of sewage.

Cyanogen

Cyanogen C_2N_2. — This compound, being endothermal, is formed in small amount when a discharge of electricity takes place between carbon poles in an atmosphere of nitrogen (compare p. 561). Cyanogen, as an endothermal substance, is more easily made as one product in an action which as a whole is exothermal (p. 372). It is prepared by allowing a solution of cupric sulphate to trickle into a warm solution of potassium cyanide. The cupric cyanide, at first precipitated, quickly decomposes, giving cuprous cyanide and cyanogen:

$$2KCN + CuSO_4 \rightarrow Cu(CN)_2 \downarrow + K_2SO_4,$$
$$2Cu(CN)_2 \rightarrow 2CuCN + C_2N_2 \uparrow .$$

Cyanogen is a very poisonous gas with a characteristic, faint odor.

Hydrocyanic Acid. — This acid, called also **prussic acid,** appears to be an equilibrium mixture of the isomeric forms HCN and HNC. Six electrons are shared between the nitrogen and the carbon atoms in the **cyanide ion** CN^-, and in hydrogen cyanide the hydrogen atom may be attached to either the nitrogen or the carbon:

$$H : C \vdots N : \rightleftarrows H : N \vdots C :$$

Hydrocyanic acid is most easily made by the action of an acid upon a cyanide (see Potassium cyanide), followed by distillation. It is a colorless liquid boiling at 26.5°. It has an odor like that of bitter almonds, and is highly poisonous. In aqueous solution it is an extremely feeble acid, and is hardly ionized at all. In consequence of this, potassium cyanide is markedly hydrolyzed by water, and its aqueous solution is strongly alkaline. The behavior of hydrocyanic acid shows it to be an unsaturated body, and the cyanide ion also is most prolific in forming complex compounds. This is presumably due to the "lone pair" of electrons on the carbon atom, which gives the ion great activity as a donor (see p. 490).

Cyanates and Thiocyanates. — When potassium cyanide is fused and stirred with an easily reducible oxide, like lead oxide PbO, the metal (for example, the lead) collects at the bottom of the iron crucible in molten form, and **potassium cyanate** KNCO is produced:

$$KNC + PbO \rightarrow KNCO + Pb.$$

Cyanic acid $H - N = C = O$ is very unstable. **Ammonium cyanate** NH_4NCO is chiefly remarkable for its transformation into urea (p. 573).

When potassium cyanide in aqueous solution is boiled with sulphur or with a polysulphide (p. 411), it is converted into **potassium thiocyanate** KNCS. This salt, or **ammonium thiocyanate** NH_4NCS, is used in testing for ferric-ion on account of the deep-red color of ferric thiocyanate (p. 908). The ammonium salt undergoes at 170° a transformation parallel to that of ammonium cyanate (p. 573), thiocarbamide (sulpho-urea) being formed.

Fulminic acid $H - O - N = C$ (p. 654) is an isomer of cyanic acid.

Exercises. — 1. (*a*) What physical property of graphite enables it to cover the surface of a stove so effectively? (*b*) How does "polishing" with a brush contribute to the result? (*c*) Why not use paint on a stove? (*d*) Explain why graphite can be used as a lubricant.

2. If a metal formed the positive electrode (anode) in electrolyzing sodium chloride solution, what chemical change might it undergo (p. 243), and which metals would be least rapidly attacked? What objection is there to using the latter metals in practice?

3. When one cubic meter of oxygen acts upon carbon, what volumes (at the same temperature and pressure): (*a*) of carbon dioxide, (*b*) of carbon monoxide, can be obtained?

4. Make equations for: (*a*) the action of sulphuric acid upon calcium carbonate; (*b*) carbon dioxide on potassium hydroxide solution; (*c*) the burning of aluminium in carbon dioxide.

5. What are the exact relative weights of equal volumes of carbon dioxide, carbon monoxide, air, and steam?

6. Why does soda water remain quiescent in the closed bottle, and why does it effervesce when the bottle is opened?

7. Formulate, in detail, the equations for the hydrolysis of (*a*) sodium carbonate, (*b*) sodium bicarbonate in aqueous solution.

8. Assuming that air contains oxygen and nitrogen in the proportion of 1 : 4 by volume, what are the theoretical proportions of carbon monoxide and nitrogen in producer gas?

9. (*a*) What volume of water gas is produced from each liter of steam, and (*b*) what are the proportions of the component gases in the product? (*c*) What impurities should you expect to find in water gas? (*d*) How should you attempt to separate the components of water gas?

10. Why is water gas an especially valuable source of heat when high temperatures are required?

11. In what respects does the action of hydrochloric acid on calcium carbonate resemble the action of the same acid, (*a*) on sodium sulphite, (*b*) on ferrous sulphide?

12. What volume of acetylene at 20° and 740 mm. is obtained by the action of excess water on 10 g. of calcium carbide?

13. What volume of carbon dioxide at 0° and 760 mm. will be obtained by the action of excess sulphuric acid on 10 g. of washing soda $Na_2CO_3,10H_2O$?

14. What volume of the same gas under the same conditions will be obtained from 10 g. of baking soda $NaHCO_3$?

15. Verify the heat absorption in the production of water gas (p. 569) from the following thermochemical equations:

$$2C + O_2 \rightarrow 2CO + 58{,}000 \text{ calories}$$
$$2H_2 + O_2 \rightarrow 2H_2O + 116{,}200 \text{ calories.}$$

16. Verify the heat effect of the reaction (p. 570):

$$CO + H_2O \rightarrow CO_2 + H_2 + 9800 \text{ calories}$$

from the above thermochemical equations and the following:

$$C + O_2 \rightarrow CO_2 + 96{,}900 \text{ calories.}$$

17. An impure sample of hydrogen contains 1.2 per cent of carbon monoxide. What volume of air (p. 453) shall we require to add to 100 liters of this gas to enable us to remove all of the carbon monoxide from it by preferential combustion (p. 571)?

18. Why is it dangerous to stay in a closed garage with the engine of your automobile running?

19. From an examination of the crystal lattice structures of diamond (p. 70) and graphite (p. 560), can you suggest reasons why the diamond is very hard and useful for grinding, while graphite is very soft and useful as a lubricant?

20. Give structural formulæ (p. 490) depicting the electron arrangements in the following molecules: carbon disulphide, carbon monoxide, carbon suboxide (p. 563).

21. What is the probable structural formula for calcium carbide (p. 563)? (*Hint:* Refer to acetylene, p. 585.)

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CHAPTER XXXIII

THE HYDROCARBONS AND THEIR DERIVATIVES. FLAME

The compounds of carbon and hydrogen are called the **hydrocarbons.** Hundreds of different hydrocarbons, containing different proportions of the two elements, are known. The natural oil *petroleum* is a mixture of many substances of this class.

The hydrocarbons fall into several distinct series, the chief one of which contains methane CH_4 as its simplest member. On account of the fact that certain members of this set are found in paraffin, it is commonly known as the **paraffin series.**

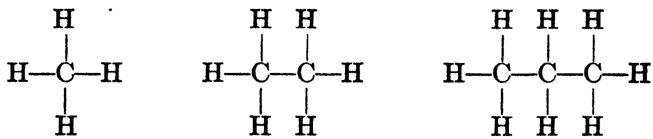
Paraffin Series of Hydrocarbons. — The following is a list of seven of the simplest hydrocarbons of this series, and of two of the higher members:

Methane CH_4	b.-p. −164°	Hexane C_6H_{14}	b.-p. 71°
Ethane C_2H_6	−89.5°	Heptane C_7H_{16}	99°
Propane C_3H_8	−37°	Hexadecane $C_{16}H_{34}$	287.5°
Butane C_4H_{10}	+1°		m.-p. 18°
Pentane C_5H_{12}	35°	Pentatriacontane $C_{35}H_{72}$	m.-p. 74.7°

After the first four, the names are based on the Greek numerals corresponding to the number of carbon atoms in the molecule. On comparing the formulæ, we observe that in each the number of units of hydrogen is equal to twice the number of carbon units plus two. The general formula is therefore C_nH_{2n+2}. Substances related in this way are said to form a **homologous series.** The series affords a striking illustration of the law of multiple proportions. We note, further, that the first four are gases at the ordinary temperature. The members of the series from pentane to pentadecane ($C_{15}H_{32}$) are liquid under ordinary conditions. From hexadecane onwards they are solids, with higher and higher melting-points.

In these compounds the carbon is quadrivalent, and each substance is related to the preceding one by containing the additional

unit CH_2. The formulæ of the first three members may be written graphically to illustrate these two facts:



Petroleum. — Petroleum is a thick, greenish-brown oil. When borings are made into the oil-bearing strata, the oil either gushes up, or is pumped to the surface. In the United States many thousands of miles of pipe-lines are used to transport the oil, with the aid of force pumps, to the refineries, and in 1935 more than 1,100 million barrels (42 gal. each) were produced. The world's production in 1935 exceeded 1,640 million barrels.

After the United States, Russia and Venezuela are the chief producers of petroleum.

Oil Refining. — The natural oil is a complex mixture, and is partially separated by distillation (p. 30) into products which are still mixtures, but are suited to special purposes. The components of lower boiling-point come off in greater proportions first and the temperature rises steadily as these components are eliminated and those of higher and higher boiling-point enter the vapor (see next section). The compounds containing sulphur which are often present, and would give the obnoxious sulphur dioxide when the oil was burned, are deprived of this constituent by heating the oil with powdered cupric oxide (Frasch process), or by adsorption on silica gel (p. 662). The unsaturated hydrocarbons (p. 584) are removed by agitation with concentrated sulphuric acid. The following are some of the products of the oil refinery:

Name	Main Components	B.-P.	Uses
Petroleum ether	Pentane, hexane	40°– 70°	Solvent, gas-making
Gasoline (petrol)	Hexane, heptane	70°– 90°	Fuel, solvent
Naphtha	Heptane, octane	80°–120°	Solvent, fuel
Benzine	Octane, nonane	120°–150°	Solvent
Kerosene	Decane-hexadecane	150°–300°	Illuminating oil

Kerosene, used in oil lamps, is usually the largest fraction of the first distillation. To be employed safely, it should not give any inflammable vapor below 65° (150° F.), which is the legal "flash-point" in many states. Formerly, efforts were made to convert the

other less valuable fractions into kerosene. Now the supply largely exceeds the demand, and special methods of treatment (see *cracking*, p. 581) are used to increase the proportion of **gasoline,** for which there is an ever-increasing need as a motor fuel.

At some suitable stage, the residual oil is chilled, and a quantity of the solid members of the series ($C_{22}H_{46}$ to $C_{28}H_{58}$) crystallizes in flakes (*solid paraffin*) and is separated by filtration in presses. **Vaseline,** $C_{22}H_{46}$ to $C_{23}H_{48}$, is separated in some refineries. **Solid paraffin** is employed for waterproofing paper, as an ingredient for candles and in making chewing gum. The final residue is used for *lubricants* and for *fuel.*

From **ozocerite,** which is a sort of natural paraffin, ceresin, a substitute for beeswax, is made. **Asphalt** is another natural mixture of solid hydrocarbons, found particularly in Trinidad, and used in road-making.

The formation of these hydrocarbons in nature is not yet thoroughly explained. One theory asserts that they are formed by the action of water upon carbides of metals; another that they result from the decomposition of vegetable or animal matter. Possibly both of these sources have contributed to their formation. Certain differences between the natural oils of different localities, such as the presence of aromatic hydrocarbons in California, point, at all events, to some difference in their origin or subsequent history.

Fractional Distillation. — When the boiling-points of two components of a liquid are very far apart, the vapor pressure of the one may be very low, when that of the other, by heating, has reached 760 mm. In this case the first distillate will contain little of the high-boiling component. When, as in the case of petroleum, the differences in boiling-points are not great, complete separation of the components is difficult. Yet by distillation in which the distillate is caught, not in one vessel, but in several successively, "fractions" are obtained such that the earlier ones contain more of the low-boiling and the later ones more of the high-boiling materials. The distillate is diverted into different vessels when the thermometer immersed in the vapor (Fig. 11, p. 30) reaches certain temperatures, or (in petroleum refineries) when the density of the distillate reaches certain values, so that fractions of the same kind are kept together. When these fractions are again distilled one at a time, beginning with the lowest, and the several distillates are divided from one another by the same methods as before, a closer approach to complete separation is effected. This process is called **fractional distillation,** and may be repeated as often as we please with constantly increasing differentiation of the fractions.

An experimental illustration may be given by mixing 0.4 c.c. of benzene (b.-p. 80.4°) with 8 c.c. formic acid (b.-p. 100°) and 2 c.c. benzyl alcohol (b.-p 206.5°), and boiling a part of the mixture in a test-tube with a small flame. The components come off in succession, and are recognized by the fact that the first and last burn with a luminous flame, while the flame of the second is non-luminous [Lect. exp.]. By passing the vapors into a condenser, and using the method described above, a complete separation can finally be made.

Oil Shale. — In Scotland, petroleum is also obtained by heating *shale*. The shale is a clay deposit, which contains no oil as such, but which when heated gives off fuel gas, ammonia (see p. 506), petroleum oils, and many valuable hydrocarbon derivatives. The richer shales yield from 30 to 40 gallons of oil per ton. The oil usually contains a much larger percentage of unsaturated hydrocarbons than well petroleum. The yield can be somewhat increased, and the proportion of undesirable unsaturated hydrocarbons diminished, by blowing superheated steam into the retorts during the distillation.

Enormous deposits of oil shale have recently been opened up in the United States, notably in Colorado, Utah, and Nevada. Though at first sight it would appear that the cost of producing oil from shale would prohibit competition with well petroleum, yet the value of the by-products offsets this disadvantage to a large extent. In any case, in view of the apprehended exhaustion of the world's petroleum fields in the near future, these shale deposits constitute a most important national asset.

Natural Gas: Methane CH_4. — Natural gas is obtained from wells, tapping strata close to those which contain petroleum, and in the same localities. It often issues under very high pressure. It owes its combustibility to its chief component (over 90 per cent), **methane** CH_4. It is largely used as a fuel in the regions in which it is found and, in the United States, the amount marketed during 1935 totalled nearly 2 trillion cubic feet. The same gas issues from many coal seams ("fire-damp"), and forms explosive mixtures with the air of mines. It rises to the surface when stagnant pools containing decomposing vegetable matter are stirred ("marsh-gas").

The formation of methane by direct union of carbon and hydrogen has already been discussed (p. 561).

Methane may be **made** from inorganic materials by the action of water upon aluminium carbide, prepared by the interaction of aluminium oxide and carbon in the electric furnace (compare p. 563):

$$Al_4C_3 + 12H_2O \rightarrow 4Al(OH)_3 + 3CH_4.$$

In the *laboratory* the gas is commonly obtained by the distillation of a dry mixture of sodium acetate and sodium hydroxide:

$$NaCO_2CH_3 + NaOH \rightarrow Na_2CO_3 + CH_4.$$

Chemical Properties of the Hydrocarbons. — The hydrocarbons, whether pure or in solution, show *no conductivity* for electricity. They have none of the chemical properties of acids, bases, or salts, and therefore do not enter into double decompositions with substances of these classes. The paraffin hydrocarbons are in fact *quite indifferent* to the presence of most chemical reagents (hence the name, from the Latin *parum*, little, and *affinis*, affinity).

All the hydrocarbons *burn* with oxygen or air to form carbon dioxide and water:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$
$$C_7H_{16} + 11O_2 \rightarrow 7CO_2 + 8H_2O.$$

The water can be shown by its condensation on a cold vessel held over the flame. The carbon dioxide gives a precipitate of calcium carbonate (p. 567) when the gases rising from the flame are drawn through lime-water.

All the hydrocarbons, when *heated strongly* (air excluded), *decompose* or **crack.** They usually lose a part of their hydrogen and become *unsaturated*. Those of high molecular weight break up to give a mixture of hydrocarbons of low molecular weight. Ethylene C_2H_4, for example, is produced in large amounts by heating the higher members of the series to a red heat. On the other hand, the lower members of the series, when heated, often give unsaturated compounds of higher molecular weight. Thus, methane gives ethylene and acetylene, along with hydrogen:

$$2CH_4 \rightarrow C_2H_4 + 2H_2$$
$$2CH_4 \rightarrow C_2H_2 + 3H_2.$$

At a white heat all the hydrocarbons decompose into hydrogen and free carbon.

The latter is deposited in a dense form called **gas-carbon,** which is used in making carbon rods for arc lights and electric furnaces, and carbon plates for batteries, and for the electrodes employed in electrolysis. The carbon is ground up, moistened with petroleum residues, subjected to hydraulic pressure and finally heated strongly to expel volatile matter.

Derivatives of the Hydrocarbons. — Although the hydrocarbons are themselves almost inert chemically, yet many important classes of organic substances may be regarded as their derivatives, one or more atoms of hydrogen in the graphic formula (p. 578) being replaced by other elements. The following tabulation should be carefully studied, and the graphic formula of each compound mentioned should be written down by the student.

1. **Halogen Derivatives.** When a mixture of methane and chlorine is exposed to sunlight several successive changes slowly occur:

$$CH_4 + Cl_2 \rightarrow HCl + CH_3Cl \text{ (methyl chloride)}$$
$$CH_3Cl + Cl_2 \rightarrow HCl + CH_2Cl_2 \text{ (methylene chloride)}$$
$$CH_2Cl_2 + Cl_2 \rightarrow HCl + CHCl_3 \text{ (chloroform)}$$
$$CHCl_3 + Cl_2 \rightarrow HCl + CCl_4 \text{ (carbon tetrachloride).}$$

Chloroform $CHCl_3$, used as an anæsthetic, and carbon tetrachloride CCl_4 (p. 562) are familiar substances. Iodoform CHI_3 is employed in surgical dressing. These substances are *not* salts, and are not ionized in solution.

2. **Hydroxyl Derivatives (Alcohols).** Water acts *slowly* upon methyl chloride, according to the equation:

$$CH_3Cl + H_2O \rightleftarrows HCl + CH_3OH \text{ (methyl alcohol).}$$

The reaction is reversible and incomplete, but can be accelerated and carried to completion by addition of a base, which removes the HCl as fast as it is formed. Ethyl chloride C_2H_5Cl gives ethyl alcohol C_2H_5OH.

Although containing the radical OH, the alcohols are *not* ionized in solution, and are therefore *not* bases. They are extensively used as solvents for other organic substances (see also p. 620).

3. **Oxygen Derivatives (Ethers).** When ethyl alcohol and concentrated sulphuric acid are heated to 140°, water and ether $(C_2H_5)_2O$ distil off. The action occurs in two stages:

$$(1)\ C_2H_5OH + H_2SO_4 \rightarrow H_2O + C_2H_5.HSO_4$$
$$(2)\ C_2H_5HSO_4 + C_2H_5OH \rightarrow H_2SO_4 + (C_2H_5)_2O.$$

Ether $(C_2H_5)_2O$ is a very volatile and inflammable liquid used as an anæsthetic and as a solvent for resins, fats and oils.

4. **Aldehydes.** By fractional combustion of methyl alcohol (passage of a heated mixture of alcohol vapor and air over a metal catalyst), formaldehyde H.CHO is obtained:

$$2CH_3.OH + O_2 \rightarrow 2CH_2O + 2H_2O.$$

Formaldehyde is a gas. Its solution in water (formalin) is employed as an antiseptic and disinfectant. Its property of hardening gelatine makes it valuable in the leather industry and in the manufacture of artificial silk. It is also used in making dyes and in the production of bakelite (p. 652). The corresponding derivative of ethyl alcohol is acetaldehyde $CH_3.CHO$. The group .CHO is characteristic of aldehydes.

5. **Acids.** By further partial oxidation, alcohols or aldehydes give members of the fatty acid series. Thus ethyl alcohol can be *oxidized* directly to

acetic acid $CH_3.COOH$ by passing a mixture of the vapor, with air, over specially prepared platinum as a catalyst:

$$C_2H_5.OH + O_2 \rightarrow CH_3.COOH + H_2O.$$

The first acid of this series is formic acid H.COOH (see p. 568), a corrosive liquid secreted by red ants and present in stinging nettles. Acetic acid (see p. 621) has many industrial uses.

The lower members of the fatty acid series are perfectly miscible with water, and are slightly ionized in aqueous solution. By neutralization with bases we obtain salts, such as the formates and the acetates. Only the hydrogen of the characteristic .COOH group (carboxyl), it must be noted, is replaceable by metals.

Oxalic acid $H_2C_2O_4$ (see p. 568) is dibasic, and consists of two carboxyl groups. Its calcium salt is the least soluble of the salts of calcium, and is found in many plants in the form of bundles of needle-shaped crystals. Potassium-hydrogen oxalate KHC_2O_4 is found in the juices of various species of *oxalis*. The acid may be made by oxidation of sugar with nitric acid.

6. **Ketones.** When calcium acetate $Ca(CH_3.COO)_2$ is heated, acetone $(CH_3)_2.CO$ distils off:

$$Ca(CH_3.COO)_2 \rightarrow CaCO_3 + (CH_3)_2.CO.$$

The ketones resemble the aldehydes in many respects, but their characteristic group :CO is not directly combined with hydrogen. Acetone is a liquid boiling at 56°, used in large quantities in the industries as a solvent.

7. **Esters.** Alcohols and acids interact slowly and incompletely to form esters. Thus when ethyl alcohol and acetic acid are used, we obtain ethyl acetate $C_2H_5.COO.CH_3$:

$$C_2H_5.OH + CH_3.COOH \rightleftarrows H_2O + C_2H_5.COO.CH_3.$$

The action may be catalyzed by the addition of a little sulphuric acid.

The equation, as given above, bears certain resemblances to a *neutralization*. It differs sharply, however, from a true neutralization in several respects. An alcohol is *not* a base, neither is an ester a salt. Both classes of substances are non-ionized in solution. True neutralization takes place instantaneously, while the foregoing action, and all like it, proceed very slowly.

The esters form the sweet-smelling constituents of plants. Many are now produced synthetically as substitutes for natural flower and fruit essences.

Organic Radicals. — In carbon chemistry there are groups of units which pass unaltered from compound to compound and receive the name **organic radicals.** They usually lack a property which inorganic radicals generally possess, namely, the power to form ions (p. 298). Methyl is such a radical, being found in methane $CH_3.H$, methyl chloride $CH_3.Cl$, methyl alcohol $CH_3.OH$, and acetic acid $CH_3.CO_2H$. Similarly we have ethyl C_2H_5 in ethane $C_2H_5.H$ and in ethyl alcohol C_2H_5OH. Methyl, ethyl, and propyl C_3H_7 are univalent radicals. We have also ethylene C_2H_4, propylene C_3H_6, and so forth, which are bivalent. Groups like NO_2 (p. 587), NH_2, CH_3CO, and many more, are other non-ionizable radicals found in organic compounds.

The above brief statements bring out a tendency which prevails in the behavior of organic substances and is almost entirely lacking in inorganic chemistry. The units may be removed from the molecule of an organic substance one by one, and other units or groups may be substituted for them without disturbing the rest of the molecule. The changes take place, not, as in the case of ionized substances, by the splitting of the molecule into two or more groups which act as wholes, but by the displacement of the units piecemeal and the introduction of new properties according to the nature of the groups introduced. Thus, if by any means we replace an atom of hydrogen by the carboxyl radical (see p. 583), the product is an acid. If we replace it simply by the group OH the product is an alcohol. Each substitution may take place repeatedly in a given molecule, so that di-basic or tri-basic acids, di-hydric or tri-hydric alcohols (see Glycerine), or substances which contain both OH and —COOH in the same molecule (like lactic acid and tartaric acid), are formed. Other groups which may be introduced or removed are $—NH_2$, $—NO_2$, —CN, etc., each of which confers upon a substance the properties which go with the group, irrespective of the other features which the structure of the substance may already present.

The student should take particular pains, at this point, to recognize the characteristic group for each class of derivatives. Thus we have, starting with ethane C_2H_6, the following series:

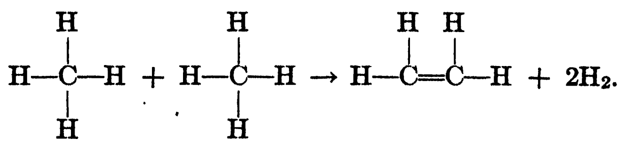
Derivative	*Characteristic Group*	*Example*
Halogen	—Cl; —Br; —I	Hexachlorethane C_2Cl_6
Alcohol	—OH	Ethyl alcohol C_2H_5OH
Ether	—O—	Diethyl ether $(C_2H_5)_2O$
Aldehyde	H—C(—)=O	Acetaldehyde $CH_3.CHO$
Acid	H—O—C(—)=O	Acetic acid $CH_3.COOH$
Ketone	>C=O	Acetone $(CH_3)_2.CO$
Ester	R—O—C(—)=O	Ethyl acetate $C_2H_5.CO.OCH_3$

Unsaturated Hydrocarbons. — In addition to the paraffin series of hydrocarbons, several other series are known in which smaller proportions of hydrogen are present. Thus, **ethylene** C_2H_4, to which illuminating gas largely owes the luminosity of its flame, belongs to a series C_nH_{2n}, all the members of which contain two atoms of hydrogen less than the corresponding compounds of the first series. Again, **acetylene** C_2H_2 is the first member of a series C_nH_{2n-2}, and **benzene** C_6H_6 begins a series C_nH_{2n-6}.

Members of the ethylene and acetylene series are found in petroleum, and are formed also to some extent by decomposition during the distillation. As oil containing them acquires dark-colored and sticky products by gradual oxidation, the oils are always refined

before being sold. They are agitated with concentrated sulphuric acid, which unites with the unsaturated substances and, being insoluble in the oil, collects in a layer below it. The oil is finally washed free from the acid with dilute alkali and with water.

Ethylene C_2H_4. — The formation of one molecule of ethylene from two molecules of methane with elimination of two molecules of hydrogen suggests its graphic formula:



Ethylene is **made** by heating common alcohol (ethyl alcohol) with concentrated sulphuric acid above 150° (contrast p. 582):

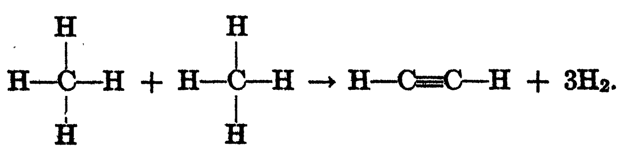
$$C_2H_5OH \rightarrow H_2O + C_2H_4\uparrow.$$

The water may also be removed by allowing alcohol to fall drop by drop on heated phosphoric anhydride. The solid metaphosphoric acid remains behind and ethylene escapes.

Ethylene is a gas which burns in the air with a highly luminous flame (see p. 591). It combines directly with bromine to form ethylene bromide $C_2H_4Br_2$.

The hydrocarbons of the ethylene series are known as *olefines*. They are of value as illuminants. Their derivatives are similar in character to those of the paraffin hydrocarbons, but are more active chemically in view of their unsaturation. When heated with hydrogen in the presence of a catalyst, such as finely divided nickel, they give the corresponding saturated derivatives (compare p. 634).

Acetylene C_2H_2. — As in the case of ethylene, the formation from methane by loss of hydrogen (p. 581) suggests the graphic formula:



Pure acetylene is prepared by the action of water on calcium carbide (p. 563):

$$CaC_2 + 2H_2O \rightarrow Ca(OH)_2 + C_2H_2 \uparrow.$$

Calcium hydroxide (slaked lime) remains. The gas *burns* with a flame even more luminous than that of ethylene. It is therefore made in generators by the foregoing action for use on bicycle lamps and for lighting buildings remote from a public supply of illuminating gas. Acetylene tanks, which are also in use, contain acetylene dissolved, under high pressure, in acetone.

The most characteristic property of acetylene is that when passed through an ammoniacal solution of a cuprous salt, it yields a red precipitate of a carbide of copper known as **copper acetylide.** The equation: $Cu_2(OH)_2 + C_2H_2 \rightarrow Cu_2C_2 + 2H_2O$, partially represents the change. This red precipitate, when dried, is extremely explosive, on account of the great amount of energy set free when it breaks up into its constituents. Its formation is used as a test for acetylene in mixtures of gases.

The Acetylene Blowpipe or Torch. — Acetylene decomposes, when heated, with *liberation* of heat:

$$C_2H_2 \rightarrow 2C + H_2 + 58{,}100 \text{ calories.}$$

When acetylene burns with oxygen, therefore,

$$2C_2H_2 + 5O_2 \rightarrow 4CO_2 + 2H_2O,$$

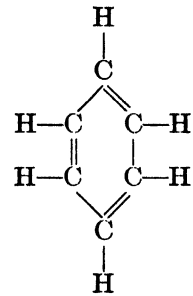
we obtain, from two g. mol. wts. of the compound (52 g.), not only the heat due to the combustion (p. 260) of the carbon to carbon dioxide (4 × 96,900 cal.) and of the hydrogen to water (116,200 cal.) but also the heat due to the decomposition of the gas (2 × 58,100 cal.). The temperature of the flame is, therefore, the highest that can be reached by the combustion of any easily obtainable gaseous mixture. The oxyacetylene flame, produced by means of a suitable burner (Fig. 73, p. 140), the gases being furnished from small portable tanks, is now used for cutting metals. Such a flame will melt its way through a 6-inch shaft of steel, or a heavy steel plate several feet wide, in less than one minute, cutting the object in two. Steel buildings have been taken apart rapidly by this device. The oxy-hydrogen torch also is remarkably efficient, when applied to the same purposes.

Benzene C_6H_6. — This is the first member of the *aromatic* hydrocarbon series. It may be synthesized by heating acetylene in a closed vessel at a moderately low temperature:

$$3C_2H_2 \rightarrow C_6H_6.$$

In practice it is obtained, with many of its valuable derivatives, as a by-product in the production of *coke* (p. 625).

The graphic formula of benzene is represented as a closed ring structure:



The hydrocarbons of the benzene series exhibit, in fact, many of the properties of *olefines,* combining directly with hydrogen and with the halogens to form saturated compounds such as hexahydrobenzene C_6H_{12} and benzene hexabromide $C_6H_6Br_6$.

The second member of the aromatic series is **toluene** $C_6H_5.CH_3$. **Naphthalene** $C_{10}H_8$ and **anthracene** $C_{14}H_{10}$ are members of more complex series, containing more than one ring.

Of all hydrocarbons, those of the aromatic series, with their derivatives, are the most important. They are of particular significance in the *dye-stuff* and *explosive* industries, and in the manufacture of synthetic *perfumes* and *drugs.* They give aldehydes, acids, esters, etc., similar to those listed under the paraffin hydrocarbons (pp. 582–3). In addition to these, the following extremely valuable classes of derivatives should be noted:

(1) **Phenols.** The substitution of hydroxyl for a hydrogen atom in the benzene ring gives phenol C_6H_5OH, a substance quite different in many of its properties from an alcohol, although it resembles the alcohols in forming esters with acids (see p. 583). Phenol, when pure, is a colorless solid melting around 40°, with a characteristic odor. It is strongly antiseptic, corrosive and poisonous. In solution it is a *weak acid.*

(2) **Nitro-Compounds.** Nitrobenzene $C_6H_5NO_2$ is obtained by the action of a mixture of concentrated nitric and sulphuric acids upon benzene in the cold:

$$C_6H_6 + HNO_3 \rightarrow C_6H_5.NO_2 + H_2O.$$

It is a pale yellow liquid, with a smell resembling bitter almonds, and is used in scenting cheap soap.

(3) **Amino-Compounds.** Reduction of nitrobenzene by a metal in acid solution gives aniline $C_6H_5.NH_2$. The amino-compounds are derivatives of ammonia, and their solutions accordingly are weakly basic. Aniline, when pure,

is a colorless, oily liquid, boiling at 185°. It is the parent substance of the countless aniline dyes.

In subsequent chapters we shall return to the different classes of organic substances, tabulated here and on pp. 582–3, and discuss their properties and industrial uses in greater detail.

Flame

We have encountered a variety of flames, from the simple one of hydrogen burning in air to the more complicated case of the luminous flame of ethylene or acetylene. The subject will now repay a somewhat closer study.

The Simple Flame. — The flame of hydrogen (giving water), or of carbon monoxide (forming carbon dioxide) is very simple in structure (Fig. 166). We find that there is a tapering column of unburnt gas in the interior, surrounded by a layer of hot gas — the flame itself. The flame is therefore a hollow cone. That the flame is hollow is easily shown by holding a wooden match across it. The match is charred at the two points at which it crosses the flame, and remains unheated in the middle. These flames are simple, because only one chemical change occurs in them. The flames are rather large, because sufficient oxygen to burn all the gas does not reach the latter at once, and the gas travels upwards and diffuses outwards a certain distance before being all consumed.



Fig. 166. Hydrogen Flame.

If oxygen is substituted for air, by lowering the jet into a jar of that gas, the flames becomes much smaller. In the absence of atmospheric nitrogen, there is now five times as much oxygen within a given range of the center of the jet as before. This chemical union, like any other, proceeds more rapidly with an increase in the concentration of the interacting substances (p. 102). It is therefore completed before the gas has time to diffuse very far from the opening of the jet.

From the chemical point of view, it is a matter of indifference whether the gas outside the flame contains oxygen, and the gas inside consists of substances ordinarily known as combustible, or whether this order is reversed. In an atmosphere of ordinary illuminating gas, the flame must be fed with oxygen (or air). This condition is easily realized (Fig. 167). The lamp chimney is closed at the top until it has become filled with illuminating gas. This can be ignited as it issues from the bottom of the wide, straight tube. When the hole in the cover of the lamp chimney is then opened, the upward draft

causes the flame of the burning gas to recede up the tube, and there results a flame fed by air and burning in coal-gas. In an atmosphere of this kind, materials playing the part of a candle burning in air would have to be substances which, under the influence of the heat of combustion, give off oxygen. Strongly heated potassium chlorate, for example, appears to burn continuously in such an atmosphere when lowered into it in a deflagrating spoon.

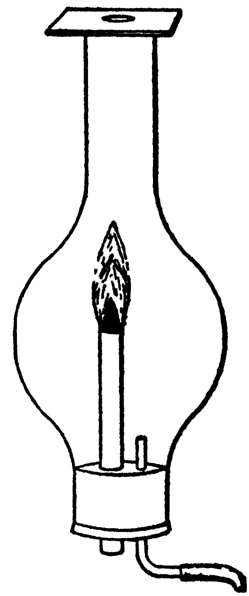


FIG. 167. Burning Oxygen in Illuminating Gas.

Luminous Flames. — The flame of hydrogen, under ordinary circumstances, is almost invisible, nearly all the energy of the combustion being devoted to the production of heat. A part of this, however, may be transformed into light by the suspension of a suitable solid body, such as a platinum wire, in the flame. The holding of a piece of quicklime in an oxyhydrogen flame (see p. 139) is a practical illustration of this method of securing luminosity. In general, luminosity may be produced by the presence of some solid which is heated to incandescence. It cannot be said, however, that no flames are luminous unless a solid body is contained in them. When compressed hydrogen is burned in an atmosphere of oxygen under pressure, the light given out by the flame is much greater, and, in general, illuminating power seems to be heightened by increase in the concentration of the gas.

In the Welsbach gas lamp the flame itself is non-luminous and, but for the mantle, would be identical with the ordinary Bunsen flame (see p. 591). The mantle which hangs in the flame, however, by its incandescence, furnishes the light. This mantle is composed of a mixture of 99 per cent thorium dioxide ThO_2 and one per cent cerium dioxide CeO_2 (see p. 836). These oxides act as a contact agent, hastening the combustion and liberation of heat close to their surface, and so acquire a temperature higher than the average for the rest of the flame. The Welsbach lamp gives ten times as much light as does an ordinary burner using the same amount of gas.

In cases of brilliant combustion, as of magnesium ribbon or phosphorus, a solid body is formed whose incandescence accounts for the light. The flame of ordinary illuminating gas does not at first

sight appear to give evidence of the presence of any solid body. But if a cold evaporating dish is held in the flame for a moment, a thick deposit of finely divided carbon (soot) is formed, and we at once realize that the light is due to the glow of these particles in a mass of intensely hot gas.

The Candle Flame. — A candle is made of a mixture of paraffin and stearic acid (one of the higher members of the fatty acid series, see p. 632). When it burns, the whole phenomenon is vastly more complicated than the burning of hydrogen. The following are some of the stages in the process, which is operated by the flame's own heat. To start with, the wax is melted and ascends the wick by capillary action. This is merely a physical phenomenon. Then the chemical changes begin. (1) The melted compounds of carbon are decomposed by the heat (*cracked*, p. 581), being turned into more volatile compounds and gases which occupy the central hollow of the flame. (2) The compounds forming the gases and vapors are further decomposed at a white heat, giving free carbon and hydrogen (p. 581). (3) All the materials finally reach a sufficient supply of oxygen and are burned to water and carbon dioxide. There are thus three chemical changes, each of which takes place in a definite region that can be observed by the eye (Fig. 168). The formation of the gases from the melted wax (without gas, there would be no flame) takes place in the dark central region where there is no oxygen. The carbon is set free and glows brilliantly in the luminous cone that surrounds the dark central region. The final combustion occurs in a fainter cone of flame covering the whole exterior.

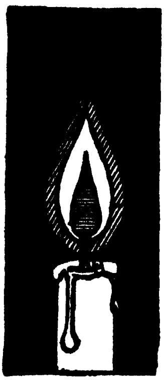


FIG. 168. Candle Flame.

That there is unburnt gas (produced by decomposition of the wax) in the center is easily shown by inserting therein a narrow tube, through which some of the gas will ascend and can be lit at the upper end. The free carbon in the luminous zone will show its presence by blackening a cold dish placed across the flame.

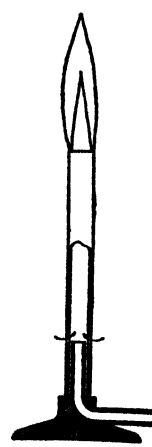
Lampblack. — In the same way, when an iron vessel, cooled by a stream of water circulating through it, is suspended in the luminous flame of natural gas or burning petroleum, the carbon (soot) is deposited on the vessel. By rotating the latter, the soot can be continuously scraped off by a stationary piece of metal. The

product, **lampblack,** mainly very finely divided carbon, is used in making printers' ink, India ink, and black varnish.

A great deal of finely-divided carbon is also obtained as a by-product in the cracking of oils, and is utilized locally as fuel.

Carburetted Water Gas. — To fit water gas, essentially $H_2 + CO$ (p. 569), which burns with a pale blue flame, for public service as an **illuminating gas,** unsaturated hydrocarbons, and particularly ethylene C_2H_4, which burn with a highly luminous flame owing to their high carbon content, must be added. The water gas is passed through a tower, filled with strongly heated brick on which oil is continually sprayed. Mixed with the vapor of the oil, the gas goes into the "super-heater," where, at a higher temperature, the decomposition into unsaturated hydrocarbons (**cracking**) takes place. The gas is then cooled and washed to remove the condensible hydrocarbons, which would otherwise collect in the service pipes with resulting waste of combustible material as well as obstruction in the delivery of the gas. A typical carburetted water gas has the composition: Illuminants (largely ethylene) 8.9 per cent; heating gases — methane 10.2 per cent, hydrogen 40.5 per cent, carbon monoxide 34.0 per cent; impurities (nitrogen and carbon dioxide) 6.4 per cent.

Carburetted water gas has now largely supplanted coal gas (p. 624) for lighting and heating purposes.


FIG. 169. Bunsen Burner.

Non-luminous Gas Flames. — When gas is to be used for **heating,** the complete combustion of the gas, without any intermediate liberation of free carbon, is desirable. This is achieved in the **Bunsen burner** (Fig. 169) by admitting air at the bottom of the burner, in such a way that the air mixes with the gas before the latter reaches the flame. When the supply of air is sufficient, the flame becomes non-luminous. With a somewhat different construction, and the use of a bellows (or compressed air) to force a large proportion of air into the gas, a still hotter flame can be produced. The instrument in this case is known as a **blast-lamp.**

The main cause of the high temperature of the **blast-lamp flame** is the more rapid stream of gas blowing past the heated body and making the "stationary layer" (p. 457) close to the surface of the latter thinner. The heat is carried by convection to this layer but

passes by conduction *through it* to the heated body. The thinner the layer, the faster will heat reach the body and the higher will be its temperature. The same "stationary layer" surrounds a dissolving crystal — the layer being in this case a saturated solution, through which the dissolving substance can pass by slow diffusion only. Violent shaking with a quantity of the solvent makes the stationary layer thinner, diminishes the distance traversed by means of diffusion, and so hastens solution.

Another reason for the higher temperature, both here and in the case of the Bunsen burner, is that although the same total amount of heat is liberated, whether the air blast is on or off, yet the non-luminous flame as a whole is *smaller in size.*

It is instructive to note the effect of forcing in larger and larger proportions of air into the Bunsen flame. The flame at the top of the tube continually diminishes in size, even after it has become non-luminous (compare p. 588). Finally, a point is reached at which the flame is so unstable that the smallest further increase in the supply of air causes it to descend into the tube. The mixture of illuminating-gas and air in the tube of a Bunsen burner is an explosive one, and the explosion-flame will proceed through it with greater rapidity, the more nearly the quantity of air approaches that required for complete combustion. When the speed with which the explosion-flame would move, equals that with which the stream of the mixed gases is coming upward through the tube, the flame reaches the unstable condition just mentioned. Any increase in the proportion of air raises the speed with which the explosion can travel, and the flame is thus able to proceed down the tube against the stream of gas. This phenomenon is frequently noticed in the Bunsen burner, when the holes admitting the air are too large, or a draft momentarily causes an increase in the supply of air. The flame **strikes back,** and thereafter continues to burn at the bottom of the tube.

The Bunsen type of burner, placed in a horizontal position (Fig. 170), is used in the ordinary **gas cooking range.** As with the Bunsen burner, some care is required to get good results. The holes which admit the air to the mixer must be kept clear of obstructions, as otherwise luminous flames are produced, smoke and soot are formed, and less heat is generated. The size of the openings must also be adjusted so that the admission of too much air will not cause the flame to flash down the burner and set fire to the gas within.

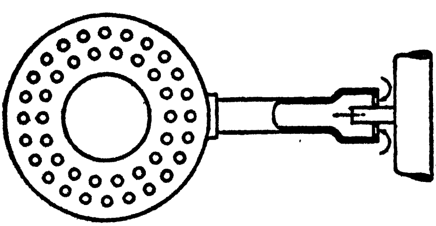


FIG. 170. Gas Cooking Range (from above).

The **Meker burner** is an improved type of Bunsen in which this striking back of the flame is prevented by a heavy metal grid clipped over the top of the burner. The principle is the same as that employed in the miner's safety

lamp, the metal carrying away the heat so rapidly that the flame is unable to pass through it.

The Causes of Luminosity and Non-Luminosity. — The study of the chemical changes taking place in the Bunsen flame, particularly with the object of explaining (1) the luminosity of the flame of the pure gas, and (2) the non-luminosity of that produced by the same gas when it is mixed with air, has been the subject of many elaborate investigations. The questions are: (1) Why is carbon liberated in the former case, and (2) why it is not liberated in the latter? Let us consider these questions in order.

1. The investigations of Lewes (1892) and others show conclusively that the free carbon in the luminous zone of the ordinary flame is accompanied by free hydrogen, and that both are formed by dissociation of the ethylene in the inner blue cone. This substance, when heated, gives acetylene, and the latter then dissociates into carbon and hydrogen (p. 581):

$$C_2H_4 \rightarrow H_2 + C_2H_2 \rightarrow 2C + H_2.$$

The carbon glows, until, as it drifts outwards, it encounters the oxygen of the air and is burned. The first oxygen encountered combines more readily with the hydrogen, since it is a gas, than with the carbon, which is now in *solid* particles and therefore burns less readily. That carbon glows when heated in the absence of oxygen, without being consumed, is a fact familiar in the behavior of the incandescent electric lamp, the filaments of which were all formerly made of carbon.

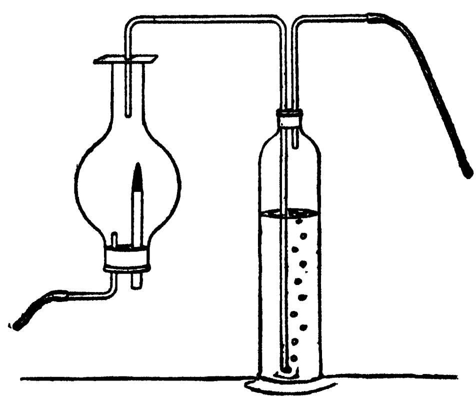


FIG. 171. Demonstration of Formation of Acetylene as an Intermediate Product in the Combustion of Illuminating Gas.

The conception that when hydrocarbons burn, they first undergo dissociation, and then union with oxygen, is in harmony with what we have observed also in the case of the combustion of hydrogen sulphide, where the presence of free sulphur and free hydrogen in the interior of the flame was demonstrated (p. 403). That acetylene is actually formed as an inter-

mediate substance is easily shown. It is found that when the Bunsen flame "strikes back," and the combustion of the gases is rendered incomplete by the contact of the flame with the cold tube, a large amount of acetylene is formed. Again, when the gases surrounding the flame of air burning in illuminating-gas (p. 589) are withdrawn by means of a pump and caused to pass through an ammoniacal solution of cuprous chloride (Fig. 171), large quantities of copper acetylide (p. 586) are precipitated.

2. The influence of the air admitted to the Bunsen burner, in interfering with this dissociation in such a way as to destroy all luminosity, is the most difficult point to explain. The effect is frequently attributed to the oxygen which the air contains. This view, however, is seriously weakened by a consideration of the undoubted fact that oxygen is not required. Carbon dioxide or steam is equally efficient when introduced instead of air (Fig. 172, coal gas enters on the left and CO_2 or N_2, from a Kipp or cylinder, on the right). Even nitrogen, which cannot possibly be suspected of furnishing any oxygen, likewise destroys the luminosity. Lewes has shown that 0.5 volume of oxygen in 1 volume of coal gas destroys the luminosity. But 2.30 volumes of nitrogen or 2.27 volumes of air accomplish the same result. Thus the efficiency of air is not appreciably greater than that of nitrogen, in spite of the fact that one-fifth of the former is oxygen.

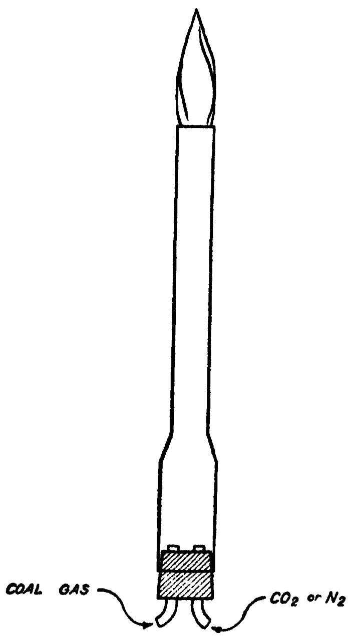


FIG. 172. Lecture Experiment to Show Disappearance of Luminosity in a Gas Flame.

It is evident that the effect is due, in part at least, to the *dilution* with a *cold* gas. This is confirmed by the observation that a cold platinum dish held in a small luminous flame is similarly destructive of the luminosity. If the tube of the Bunsen burner is *heated,* so that the mixed gases are considerably raised in temperature before reaching the non-luminous flame, the latter becomes luminous. It is probable, therefore, that the cold gas lowers the

temperature of the inner flame, and at the same time the dilution diminishes the speed with which the free carbon is formed (Lewes). Even if the temperature is not reduced below that at which dissociation of the ethylene can occur, yet the dilution and cooling, together, prevent that sharp dissociation at this particular point which is necessary for the production of the great excess of free carbon needed to furnish light.

Before these investigations were made, a different answer was given to the question why the flame of pure illuminating gas contains free carbon and is luminous. It was said that hydrogen was more easily burned than carbon, and therefore the latter was left free, to be burned later. It is true that gaseous hydrogen burns more easily than *solid* carbon, *e.g.*, charcoal. But in ethylene, *both* elements are equally gaseous and the explanation is faulty. Smithells (1892) demonstrated the falsity of this explanation by devising a **cone-separator** (Fig. 173). The air and ethylene or other gas are admitted in proportions which can be varied, and the mixture burns at the top of the wider tube. As the quantity of air is increased, however, the speed with which an explosion-flame would pass through it becomes greater, and finally the inner cone passes down and rests upon the mouth of the narrow tube through which the mixture of gases is issuing more rapidly. A preliminary combustion takes place in the blue cone, while the final conversion of the whole material into carbon dioxide and water is completed in the outer mantle. This remains at the top of the wider tube, where alone the necessary air can be obtained. By means of a side tube (not shown) Smithells withdrew the interconal gas and found that, while all of the carbon was burned by the inner cone as far as carbon monoxide CO, most of the hydrogen was still entirely uncombined. This was the case, not only with illuminating-gas, which initially contains much free hydrogen, but also when the flame was fed with *pure methane*. The change in the inner cone of the Bunsen flame consists, therefore, mainly in the burning of all the hydrocarbons to carbon monoxide, with liberation of the hydrogen. In the outer cone, it is practically a burning of water gas that is taking place.

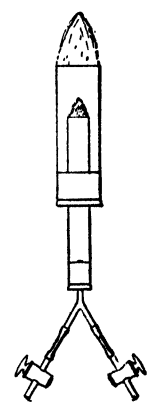


FIG. 173. Smithells' Cone-Separator.

Exercises. — 1. When vegetable matter decays in the air the carbon it contains is finally all turned into carbon dioxide. When the same matter decays under water, it gives methane (p. 580). Explain the difference in the result.

2. What is the density (air = 1) of (*a*) methane, (*b*) ethylene?

3. Write the graphic formulæ for propane, propyl chloride, propyl alcohol, dipropyl ether, propionaldehyde, propionic acid, dipropyl ketone, propyl propionate.

4. Write the graphic formulæ for toluene, phenol, nitrobenzene, aniline.

5. (*a*) Given a flame of hydrogen burning in a jar of air, what would be the effect on the flame of lowering the pressure of the air by means of an air pump? (*b*) What would be the effect on the average temperature of the

flame? (*c*) How about the heat produced by burning 1 g. of hydrogen in each case? (*d*) What differences would be observed in using an alcohol lamp at the bottom and on the top of a high mountain?

6. (*a*) In the candle or gas flame, what is the source of the light? (*b*) Why does such a flame become smoky when placed in a draft?

7. When benzyl alcohol vapor $C_6H_5.CH_2OH$ burns in oxygen, what are the volume relationships between the reacting substances and the products of the interaction?

8. What weight of aluminium carbide would you require to add to excess water to obtain 50 liters of methane at 15° and 740 mm.?

9. A cold porcelain dish is held in a jet of burning hydrogen sulphide for a few seconds (Fig. 122, p. 403). What do you observe? Does this prove that hydrogen is more combustible than sulphur?

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CHAPTER XXXIV

PLANT LIFE. CELLULOSE, STARCH AND SUGAR

Plants and animals are similar in composition. They contain much the same elements, and these are present in the form of similar compounds. They differ sharply, however, in the foods they use in constructing these compounds. Plants use simple, inorganic materials; animals absolutely require complex, organic substances as food. The main chemical processes, therefore, are very different in the two groups.

How the Plant Feeds. — The walls of the cells which form the framework of a plant are made of **cellulose** $(C_6H_{10}O_5)_y$. In the cells, especially in certain parts of the plant, granules of **starch** $(C_6H_{10}O_5)_x$ are found. These complex substances differ in properties, although they have the same composition.* The plant juice (sap) contains **sugars,** such as cane-sugar or sucrose, $C_{12}H_{22}O_{11}$, in variable amounts, and also **esters** (*vegetable oils*, p. 632) and **alkaloids** (*vegetable bases*, p. 650) in much smaller quantities. The plant cells also contain still more complex substances, known as **proteins.** *Gluten,* the sticky portion of wheat flour (p. 8), is a typical protein. These proteins are the chief components of the protoplasm, a semi-liquid substance lining each active plant-cell, and the real seat of life of the plant. Now all these substances contain carbon, hydrogen, and oxygen, and plant food must furnish these elements, which constitute over 95 per cent, on the average, of all plants. Hence, in addition to large quantities of water ascending from the soil through the roots and stem, and sufficient amounts of compounds of nitrogen, potassium, phosphorus, and other elements, all plants require an abundant supply of carbon in absorbable form. This carbon is practically all taken up by

* Since neither cellulose nor starch can be vaporized without decomposition, and since they do not form true solutions in any of the common solvents, we have no means of determining their exact molecular weights, and are therefore forced to write their formulæ in the indeterminate forms $(C_6H_{10}O_5)_y$ and $(C_6H_{10}O_5)_x$ respectively. The molecule in each case is certainly exceedingly complex.

plants in the form of atmospheric carbon dioxide. It is admitted through minute openings (stomata), situated mainly in the surface of the leaves.

The Reactions Involved. — Comparison of the formulæ of carbon dioxide CO_2 and of any plant substance, like starch $(C_6H_{10}O_5)_x$, shows at once that the latter contains a far smaller proportion of oxygen, relative to the amount of carbon, than does the former. Hence, during the digestion or assimilation of the carbon dioxide by the plant, this compound must be *reduced*. In point of fact, the chlorophyll (green coloring matter) and protoplasm in the leaves act upon the carbon dioxide, causing oxygen to be liberated:

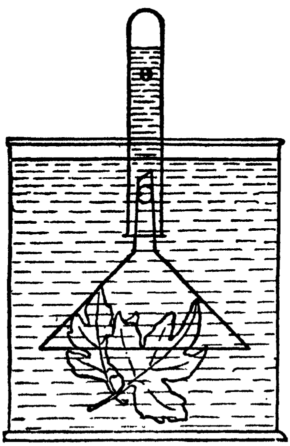


FIG. 174. Liberation of Oxygen from a Plant in Sunlight.

$$6CO_2 + 5H_2O \rightarrow C_6H_{10}O_5 + 6O_2 \uparrow .$$

This action goes on only in the sunlight. The steps by which sugar, starch, and cellulose are manufactured by the plant, out of water and carbon dioxide, are not yet perfectly understood. But the liberation of the oxygen is easily shown by placing a green plant under water in a jar, and setting the jar in the sunlight (Fig. 174). Bubbles of gas appear on the leaves, grow larger, and then detach themselves and rise to the top. The gas relights a glowing splinter of wood, and is pure oxygen.

The results of recent investigations suggest the following stages of the reaction:

(1) Carbonic acid, formed by the union of water and carbon dioxide, is *reduced* to formaldehyde (p. 582), oxygen being liberated:

$$H_2CO_3 \rightarrow H.CHO + O_2.$$

(2) Formaldehyde molecules quickly combine together, or *polymerize*, to give simple sugars with the formula $C_6H_{12}O_6$:

$$6H.CHO \rightarrow C_6H_{12}O_6.$$

(3) These sugars lose a molecule of water, and *polymerize* further to form starch and cellulose:

$$nC_6H_{12}O_6 \rightarrow nH_2O + (C_6H_{10}O_5)_n.$$

Reactions (1) and (2) have been carried out in the laboratory under the influence of ultra-violet light. Chlorophyll thus appears to act in the rôle of a *promoter* (compare p. 570), in the presence of which the reactions are able to proceed in visible light.

Reverse reactions also take place in the plant. Thus starch, which first accumulates in the leaves, is later turned back into a sugar soluble in the sap, and is then able to pass to parts of the plant requiring new material. Some carbon dioxide is also liberated from plant surfaces by oxidation of sugars.

The Thermochemistry of the Reaction. — In the combination of carbon and oxygen, during combustion of wood or coal, much heat is liberated. Hence, when oxygen is taken out of carbon dioxide again, heat or energy in some form must be *supplied.* When this takes place in a plant, the energy is evidently furnished by the sunlight, for the action proceeds more slowly in the shade, and ceases in the dark.

The energy required can be measured, and may be expressed in calories. The energy required to produce one simple formula-weight of cellulose ($C_6H_{10}O_5 = 162$ g.) is 671,000 calories. The whole may be represented in a rough equation, in which the intermediate steps are left out, and only the starting substances and the final products are shown:

$$6CO_2 + 5H_2O + 671{,}000 \text{ cal.} \rightarrow C_6H_{10}O_5 + 6O_2.$$

Photochemical Action. — We have seen that light may frequently act catalytically, as on a mixture of hydrogen and chlorine (p. 243) or an aqueous solution of hypochlorous acid (p. 371). These actions involve the *liberation* of energy and go on spontaneously (compare p. 259) under proper conditions. On the other hand, light (radiant energy) may actually be *absorbed* in large amount in producing a chemical change, as in decomposing silver chloride (p. 253), or in the above instance. All wave lengths of light, which is the same as to say all colors of light, are not equally active in any one case. **But there is no particular set of wave lengths which is of special chemical activity.** In the action on silver chloride, green and blue light is very active, while red is almost without effect. Here, in the actions in which chlorophyll is concerned, it is the red and yellow light that produces the chemical change, and a plant exposed to blue light (*e.g.*, by shading with blue glass) will assimilate none of the carbon dioxide in the air surrounding it. The chemical substances in the retina of the eye seem to resemble those in the leaves of plants, for they are most affected by red and yellow light. To put this another way, a spectrum of uniform intensity throughout, when viewed by a plant or a human eye, would appear to be brightest in the red and yellow portions, while a considerable stretch towards the blue extremity would actually be invisible. On the other hand, to an eye in which the active substance was silver chloride, if such an eye could be imagined as existing, the red end would be invisible and the blue and ultra-violet would be the most brilliant parts.

Cellulose $(C_6H_{10}O_5)_y$. — This substance, named cellulose because it forms the walls of the cells, composes much of the framework and intricate structure of plants. We are familiar with pure cellulose in the forms of **filter paper** and **cotton.** The latter consists of fine, hollow tubes of cellulose (see *A*, Fig. 187, p. 647), large tufts of which surround the seed of the cotton plant. **Linen** is almost pure cellulose, **wood** is largely cellulose, and **paper pulp** is practically all cellulose.

Cellulose *interacts* with very few chemical substances. It is because it thus remains unchanged by most substances that come in contact with it, that it can be used as a filter paper. When it does undergo chemical change, it acts as if it contained hydroxyl (OH) groups, and behaves therefore chemically like an alcohol (see p. 651), forming valuable derivatives (explosives and plastics) which will be discussed later (Chapter XXXVIII).

Paper Manufacture. — Paper is, as mentioned above, practically pure cellulose $(C_6H_{10}O_5)_y$ and is made from a mixture of cotton or linen pulp and wood pulp — the cheapest varieties from the latter alone. The wood is cut into chips and heated ("cooked") with a solution of calcium bisulphite $Ca(HSO_3)_2$. This dissolves out the **lignin,** which, together with cellulose, makes up the solid part of its structure. The pulpy material is then washed, beaten with water to reduce it to minute shreds, and bleached with very dilute chlorine-water. The pure cellulose, now paper pulp, suspended in water, is spread on screens, drained, pressed, and dried. During the process other substances are usually added. Thus size (glue or gelatine) prevents the ink from running; pulverized calcium sulphate (gypsum), and other white solids ("loading") give body to the paper and make possible the subsequent production of a smooth surface by rolling ("calendering"). Ultramarine (blue) and other colored powders are added to the pulp when special tints are required.

Other Uses of Cellulose. — Cellulose dissolves in hot, concentrated zinc chloride solution. When the liquid is pressed through a small orifice into alcohol, the cellulose is reprecipitated in the form of a thread. By carbonizing, this is made into **filaments** for incandescent electric lamps (now largely replaced by tungsten, see p. 883).

Cellulose is soluble also in a solution of cupric hydroxide in excess of ammonium hydroxide, and is reprecipitated by dilute

sulphuric acid. Paper or cotton goods can be passed through first one and then the other of these liquids, and so receive a tough, **waterproof** surface. **Artificial silk** (or **rayon**) is made by pressing the solution through dies into the precipitant. It can be dyed to any desired tint, and is at least as brilliant in appearance as the natural article. Its strength, however, does not equal that of the natural silk fibre, especially when wet.

Cotton, when dipped in concentrated sodium hydroxide solution, and then stretched while drying to prevent the shrinkage which otherwise occurs, acquires a brilliant luster and is used in enormous quantities under the name of **mercerized cotton.**

Finally, mercerized cotton, or wood pulp treated with caustic soda, combines with carbon disulphide to give **viscose.** Viscose dissolves in water, and decomposes in solution giving a plastic form of cellulose. This can be rolled into transparent sheets, made into caps for bottles, molded into any form, or pressed through dies into solutions of salts of ammonium to give another form of rayon. It may be noted that, of the total production of 260,000,000 pounds of artificial silk in the United States, in 1935, 75 per cent was manufactured by the viscose process.

Starch $(C_6H_{10}O_5)_x$. — Starch is found in plants in little *colorless granules* of various rounded shapes (Fig. 175) which may readily be seen under the microscope. These granules are massed in large numbers in the ears of wheat and oats, in the tubers of potatoes, in the grains of maize (corn) and in peas and beans. Even in the leaves they can be seen, immediately after the plant has been exposed to sunlight. They gradually disappear from the leaves in the dark. They can be recognized, not only by their appearance, but, without a microscope, by the **iodine test.** When a drop of potassium iodide solution, rendered brown by the addition of a little free iodine, is placed on the leaf or other part of the plant, the granules of starch become *blue* (compare p. 7) while the other parts are not affected.



FIG. 175. Starch Granules.

Preparation of Starch. — If flour, which is made by grinding wheat, and is three-fourths starch, is placed in a muslin bag and kneaded under water, the granules of starch are washed out and render the water milky (p. 7). After a time the granules settle

and the water can be poured off. Starch is manufactured by washing disintegrated potatoes (in Europe) or maize (in America) on sieves, and collecting and drying the white powder deposited in the water used for the washing.

Starch is *not soluble* in water. If it is boiled with water, however, the granules swell and break, and the starch becomes freely diffused through the water, forming a clear liquid. With little water, a sort of transparent jelly is produced. When the liquid is poured through a filter, a large part of the starch goes through the paper as if it were truly dissolved. Such a state is called a **colloidal suspension** (p. 198). Imitation solutions like this are constantly met with in using complex organic compounds such as enter into jellies, glues, soaps, and the juices of the bodies of animals. Even inorganic substances, of the insoluble class, may give suspensions. A description of their peculiarities must be noticed under soap (pp. 641-2).

The colloidal suspension of starch is *used* in the laundry, for stiffening white goods. Glucose is manufactured from it.

Glucose $C_6H_{12}O_6$ from Starch. — When starch is boiled with water, to which a few drops of an acid (catalyst) such as hydrochloric acid have been added, the liquid, after neutralization of the acid, is found to be sweet in taste. A kind of sugar, **glucose** $C_6H_{12}O_6$, can be obtained in crystals by evaporation. In commerce the evaporation is stopped before crystallization begins, and the syrup ("corn-syrup," if maize is the source of the starch) is sold for making candy and for preserving fruits:

$$(C_6H_{10}O_5)_x + xH_2O \rightarrow xC_6H_{12}O_6.$$

Glucose is known also as **dextrose** and as **grape sugar.** Brownish crystalline granules found in dried grapes (raisins) are mainly composed of it. When pure, it is almost colorless. It *reduces* cupric hydroxide, in Fehling's solution (see p. 791), to red cuprous oxide.

An intermediate product in the hydrolysis of starch is **dextrin,** used as paste or mucilage. Corn syrup contains 30–40 per cent of unchanged dextrin, 40–50 per cent of glucose, and the rest water.

The Sugars. — The common sugars are divided into two classes. There are several sugars, having the same composition, $C_6H_{12}O_6$, but different structural formulæ and consequently different prop-

erties, which are called **monosaccharides.** Other sugars, having twice as many carbon units in the formula $C_{12}H_{22}O_{11}$, are called **disaccharides.** The sugars we have occasion to mention here are the following:

Monosaccharides:	**Glucose** (dextrose or grape sugar)
	Fructose (laevulose or fruit sugar)
Disaccharides:	**Sucrose** (cane-sugar, beet-sugar, saccharose)
	Maltose (formed by action of malt on starch)
	Lactose (milk-sugar, found only in animals).

Since cellulose, starch and the sugars are freely changed, one into another, they are grouped together in one class, the **carbohydrates.** The word refers to the fact that they contain hydrogen and oxygen in the proportions required to form water, and are, therefore, in a sense, hydrates of carbon. When dehydrating agents like concentrated sulphuric acid (p. 427) act on the carbohydrates, a black mass of carbon is left.

Sucrose or Cane-Sugar, $C_{12}H_{22}O_{11}$. — The sugar-cane and the beet produce exceptionally large amounts of this sugar, which is the one commonly used as table sugar. Maple sugar, obtained by evaporating the sap of the tree, is composed mainly of the same substance.

The sugar-cane forms stalks from ten to twelve feet high. The juices are extracted by crushing the plants between rollers. The liquid is evaporated in closed pans. A vacuum maintained in the pans permits the boiling of the solution at a low temperature (about 65 degrees) and prevents the decomposition of a part of the sugar which would otherwise occur. When the syrup cools, the sugar crystallizes and the crystals are freed from the liquid in the centrifugal machines. The crystals are brown in color. At the sugar refinery they are dissolved, and the solution is passed through a column of bone charcoal. This adsorbs (see p. 623) the coloring matter, and the filtrate is once more evaporated and allowed to crystallize.

The sugar beets, which contain 16 per cent or more of cane-sugar, are sliced and steeped in water to extract the sugar. The liquid contains gummy material in colloidal suspension. This is coagulated and precipitated by adding "milk of lime" (calcium hydroxide $Ca(OH)_2$ suspended in water) and boiling. Carbon

dioxide is then passed through the solution to precipitate the excess of lime:

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 \downarrow + H_2O.$$

The solution is decolorized with charcoal and evaporated to crystallization in the same way as is the extract from the sugar-cane.

Properties of Sucrose. — Sucrose *crystallizes* in four-sided prisms, the form of which (Fig. 26, p. 61) is seen in "rock-candy." It *melts* at 160°. It does *not* reduce Fehling's solution (p. 791). When heated to 200° it begins to decompose, slowly losing water and leaving a brown, soluble mass called **caramel,** used in coloring whiskey and soups.

When boiled with water, to which a trace of an acid catalyst has been added, it is *hydrolyzed,* giving a mixture of the two monosaccharides, glucose and fructose:

$$C_{12}H_{22}O_{11} + H_2O \rightarrow C_6H_{12}O_6 \text{ (glucose)} + C_6H_{12}O_6 \text{ (fructose)}.$$

This mixture of glucose and fructose is called **invert sugar** and is found in many sweet fruits and in honey. Each sugar interferes with the crystallization of the other, by lowering the freezing-point (p. 285), and so invert sugar is added in making "fondant" candy and candy that is to be "pulled," both of which are intended to remain soft for some time. With the same object in view, vinegar, lemon juice, or cream of tartar is added to a syrup made from cane-sugar, in order that the acid contained in them may produce some invert sugar and so give a less crystalline mixture (icing for cakes). Prolonged heating has the same effect.

The action of the acid in the hydrolysis or **inversion** of sucrose is catalytic, and the rate of this more or less leisurely chemical change depends upon the concentration of the hydrogen ions. It therefore furnishes one means of comparing acids as regards their chemical activity, and has the special advantage that the acid is not consumed during the process but remains of constant concentration throughout the whole time.

Exercises. — 1. What inference do you draw as to the composition of tapioca, sago, and rice from the facts that they are plant products and when boiled with water and cooked give a jelly-like mass? How should you confirm your inference?

2. (*a*) Why does a concentrated solution of sugar boil at a temperature far above that of boiling water? (*b*) In evaporation why is the boiling-point lower in a vacuum than in air?

3. In what relative volumes are carbon dioxide used and oxygen produced by a plant?

4. What products must be formed when paper is burned? Make the equation.

5. An organic substance gives, on analysis, the empirical formula $C_6H_{10}O_5$. How would you proceed to determine whether it is starch or cellulose? Give as many distinctive tests as possible.

6. How would you distinguish between sucrose and glucose? Give as many methods as you can.

7. 10 g. of a carbohydrate give, on complete combustion in air, 15.43 g. of carbon dioxide and 5.79 g. of water. What is its formula?

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CHAPTER XXXV

PLANT GROWTH. OSMOSIS. FERTILIZERS.

For successful growth, plants require carbon, hydrogen, oxygen, phosphorus, potassium, nitrogen, sulphur, calcium, iron, and magnesium. The carbon is chiefly supplied by the carbon dioxide in the air, as we saw in the preceding chapter. Water supplies hydrogen and oxygen, entering through the leaves, and also through the roots and stems. Oxygen is also supplied directly by the air. Phosphorus, nitrogen, and sulphur are absorbed from the soil by the roots as soluble phosphates, nitrates, and sulphates, and nitrogen sometimes as ammonia. Potassium commonly enters as carbonate or bicarbonate. Calcium and magnesium are absorbed as phosphate, nitrate, sulphate, or bicarbonate; and iron as ferric hydroxide ($Fe(OH)_3$). Manganese, chlorine and silicon are also present in many plants. In a few species, sodium salts can take the place of potassium salts.

The last-named elements are used in such small amounts, relative to the available supply in the soil, that they rarely need attention. **Nitrogen, phosphorus, potassium** and **calcium,** however, the presence of which in quantity is essential to the life and development of plants, often need to be added to soils which are deficient in these elements. Suitable compounds are therefore used in enormous quantities as fertilizers.

Before discussing individual fertilizers, we may profitably take up the general question of how the plant derives its food from the soil.

How the Plant Feeds. — We have mentioned (p. 597) that the plant juice or sap contains soluble sugars, which travel to those parts of the plant which require new material for their growth. The moist walls of the root-hairs of the plant are freely permeable to *water,* the entrance of which into the plant from the soil is necessary to offset evaporation from the leaves and stems. Soluble salts present in the soil water are also able to pass, although less freely, and are incorporated in the sap. If they are of nutritive value to the plant, they react, as they circulate through the plant from

cell to cell, with the organic constituents there present, forming more complex compounds, which are unable to permeate the boundary walls of the cells, and thus become permanently fixed in the growing parts. If they are not of nutritive value, they complete the circuit unchanged.

Now the passage of salts from the soil water into the plant continues only until the sap inside contains the same concentration of each salt as the solution outside. Hence while *nutritive* constituents, which are removed from the sap during its circulation through the plant, can continuously enter to keep up the supply necessary for growth, *non-nutritive* constituents soon reach their equilibrium concentration and are thereafter rejected.

Osmosis. — The membranes lining the cell walls and the root-hairs of plants exercise, as we saw above, a *selective action* with regard to the passage of different substances through them. Water is able to permeate the membranes quite freely, dissolved salts pass through less readily, while the movement of complex organic substances, such as proteins, is completely blocked. Upon this selective flow of materials through the plant membranes, it must be noted, the life of a plant is absolutely dependent. If the membranes were freely permeable to the organic materials contained in the plant sap, the plant would soon lose these materials to the outside soil and die of exhaustion.

The selective flow of certain components of a solution through a membrane is known as **osmosis**. Osmosis and its consequence, **osmotic pressure**, are phenomena which may be very clearly illustrated in the laboratory by means of a solution of cane sugar and an artificial membrane of precipitated cupric ferrocyanide $Cu_2.Fe(CN)_6$.

Professor Crum Brown has devised an arrangement which exhibits the action of a perfectly semi-permeable membrane very strikingly [Lect. exp.]. A concentrated solution of calcium nitrate is shaken with a small amount of phenol (p. 587), so as to become saturated with the latter, and the mixture is then poured into a tall, narrow cylinder. The phenol rises and floats upon the surface of the calcium nitrate. The amount of phenol should not be more than sufficient to saturate the liquid and give a residual layer a few millimeters in thickness. Distilled water, also saturated with phenol, is cautiously introduced above all. The water on both sides of the layer of phenol is soluble in phenol, and consequently, by dissolving in this and passing out on the other side, can traverse the partition. The calcium nitrate, however, which is here the dissolved substance, cannot traverse the phenol, in which it is not soluble. The phenol therefore constitutes a perfect semi-permeable membrane. If the level of the lower side of the phenol is marked on the outside of the cylinder

by means of a strip of paper, it will be found, as the arrangement is watched from day to day, that the water passes through the phenol into the solution, and the phenol rises higher and higher, until finally it surmounts all the rest of the liquid.

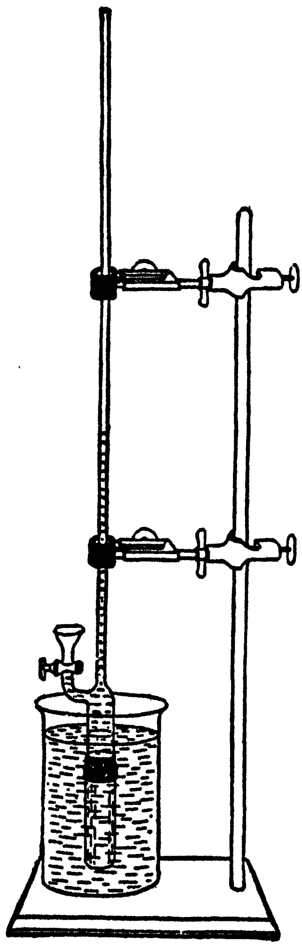


FIG. 176. Osmotic Pressure Cell.

Osmotic Pressure. — A suitable *semi-permeable membrane* for use in the measurement of osmotic pressure may be obtained by soaking a clean porous pot in a solution of potassium ferrocyanide $K_4.Fe(CN)_6$ (p. 907), rinsing in water, and then allowing to stand in a solution of cupric sulphate. The diffusion of the latter substance into the cell produces, by double decomposition, a film of insoluble copper ferrocyanide within its walls. This film is freely permeable to water molecules, but not to molecules of sugar dissolved in the water.

A simpler method is to use a *diffusion shell* of specially treated parchment, of test-tube form. This, however, is not entirely impermeable to sugar molecules.

The porous pot or diffusion shell, filled with sugar solution, is securely attached to a long glass tube, and suspended in pure water (Fig. 176). It is found that the level of the liquid in the tube gradually rises until, if the membrane remains intact and is truly impermeable to sugar, a definite hydrostatic pressure is established, the magnitude of this **osmotic pressure** depending only upon the *temperature* and upon the *fraction of sugar molecules in the solution* within the cell.

The preparation of a membrane of sufficient strength, and possessing the maximum permeability with respect to water and the minimum permeability with respect to dissolved substances, presents great difficulties. The best membranes are obtained by using a current of electricity to cause the cupric ions to move into the wall of the cell on one side and the ferrocyanide ions to move towards them from the other side.

Explanation of Osmotic Pressure. — For a complete discussion of osmotic pressure, the reader is referred to a *modern* text-book of physical chemistry. A brief explanation by means of the molecular hypothesis, however, may be given here.

The molecules of water in the pure water outside the cell, and the molecules of water and of sugar in the solution inside the cell, are all in rapid motion (p. 203). When, in consequence of this motion, they strike the membrane, water molecules have a chance of passing through, but sugar molecules are all turned back. Now the concentration of water molecules in the pure water *outside,* striking the membrane and attempting to enter the cell, is *greater* than the concentration of water molecules in the solution *inside,* striking the membrane and attempting to leave the cell (compare vapor pressure, p. 212). Hence more water molecules will be entering than leaving, and the level of the liquid inside the tube must rise in consequence.

Why does the level of the liquid stop rising when a definite hydrostatic head has been established? Because now, although there is still a greater concentration of water molecules in the pure water outside than in the solution inside, water molecules attempting to enter the cell through the membrane are *opposed* by the hydrostatic pressure, while water molecules attempting to leave are *assisted* in their passage. We have on one side of the membrane *more* water molecules with a *smaller* chance of getting through, on the other side *fewer* water molecules with a *greater* chance of getting through. Equilibrium is reached, evidently, when these two factors counterbalance.

The student should note very carefully the fact that *the sugar molecules are not directly concerned in the phenomenon of osmotic pressure.* Their function is merely to *reduce the concentration of water molecules* in the solution inside the cell. Any solute, with respect to which the membrane is similarly impermeable, will give the same effect, the osmotic pressure at any given temperature being dependent only upon **the fraction of solute molecules in the solution,** that is, upon the extent to which the concentration of *water* molecules has been reduced (compare, again, vapor pressure depression of solutions, p. 214).

A solution containing 1 g. molecular weight of an inert solute dissolved in 1000 g. water should give at 20°, with a perfectly semi-permeable membrane, an osmotic pressure of 23.6 atmospheres.

Osmotic Pressure and the Gas Laws.—It may be shown, by the use of thermodynamics, that the osmotic pressure of an exceedingly dilute solution is, under certain assumptions, practically identical with the gaseous pressure which the solute would exercise if the solvent were suddenly annihilated and the solute were to exist, in the space formerly occupied by the solution, in the state of a gas. This fact, first demonstrated by Van't Hoff in 1885, has led many chemists to consider osmotic pressure an exact analogy of gaseous pressure and to assume that the gas laws are fundamentally applicable to dilute solutions. Such a point of view proved, indeed, of extreme value in the early theoretical development of the properties of solutions. Unfortunately, however, the tendency to press the analogy too far (*e.g.*, to postulate that the osmotic pressure is due to the bombardment of the membrane by pseudo-gaseous solute particles) was seldom resisted.

It cannot be too strongly emphasized that osmotic pressure bears no direct relation at all to gaseous pressure, and the true osmotic pressure equation is quite distinct from any possible gas equation. The laws for a *perfect gas* are represented by the statement: $PV = RT$ (where P is the pressure, V the volume occupied by one gram-molecular weight of the gas, T the absolute temperature and R a constant). The osmotic pressure equation for an *ideal solution*, omitting a small correction for compressibility, may be written: $\pi V = RT \log_e x$ (where π is the osmotic pressure, V the volume occupied by one gram-molecular weight of the *solvent*, and x the molecular fraction of the *solvent* in the solution). This admittedly reduces to the perfect gas equation when the solution is infinitely dilute, but the student with any knowledge of mathematics will recognize that two functions may possess the same limiting value without being related in any way. As has been shown in the preceding section, it is the solvent, not the solute, that is directly concerned in the phenomenon of osmotic pressure, and any attempt to correlate the properties of solutions of finite concentration with the gas laws, neglecting the solvent entirely, is certain to lead to confusion.

According to the modern viewpoint, any solute in a liquid solution must be assumed to exist, however great its dilution, not in the gaseous but in the liquid state (see p. 214).

Osmotic Pressure in Plant Life.—Osmotic pressure was first studied by Pfeffer, a botanist, in 1877. De Vries (1878) used plant cells for the same purpose. The cells included a liquid containing various salts in solution, and a protoplasmic layer which lined, but was not firmly attached to, the cell wall. This protoplasmic layer behaved like an imperfect semi-permeable membrane. When such cells were immersed in a concentrated solution of any substance, the water passed from the interior of the cell to the solution, and by means of a microscope a shrinkage of the protoplasmic layer away from the cell wall could be observed. Conversely, when such cells were placed in pure water, or a solution of a very dilute nature, water passed from the outside into the interior, and the protoplasmic layer was distended so as to cause the cell to become turgid.

Osmotic pressure is, therefore, a subject of great interest in connection with the physiology of plants. It aids in explaining why a withered flower, containing a solution in its cells, revives when placed in pure water. The latter enters through the walls of the cells, and the pressure thus produced distends the structure and stiffens it. Similarly, the wilting of plants, when too high a concentration of salts as fertilizers is added to the soil, is explained. In the animal body also, osmosis plays a very significant part.

Fertilizers. — Many soils are either naturally deficient in one or more of the necessary plant foods, or the supply may have been exhausted by repeated cropping. Every crop removes permanently a certain part of the supply. This is shown in the following table, which gives a comparison of the amounts of nitrogen, phosphorus and potassium removed from an acre of land by the sugar cane, sugar beet and certain other common crops:

Kind of Crop	Yield per Acre	Nitrogen, Lbs.	Phosphorus, Lbs.	Potassium, Lbs.
Sugar Cane	20 tons	40	6	81
Sugar Beet	10 "	30	6	58
Tobacco	1600 lbs.	76	7	166
Corn	40 bushels	56	9	19
Wheat	20 "	41	6	14
Oats	40 "	40	6	27
Barley	30 "	56	7	42
Clover Hay	2 tons	82	8	73

When the supply becomes reduced, the crops become poor. Moreover, the necessary elements must be present in *soluble form,* or they cannot enter into the plant system.

Feldspar $KAlSi_3O_8$ is a common component of many rocks, such as granite (p. 6). When such rock material, contained in the soil, is decomposed by *weathering,* through the action of carbonic acid from the atmosphere, the feldspar gives *clay* $HAlSiO_4$ and soluble compounds of potassium. There are immense quantities of feldspar available, but the process of weathering is very slow, and in many agricultural regions the soil is therefore deficient in soluble salts of potassium.

It is just as necessary to feed crops as to feed cattle, and equally foolish to starve either of them. Fertilizers are used to make good the original, or acquired deficiencies of the soil in the most important elements, *nitrogen, phosphorus, potassium* and *calcium.* It is absolutely necessary, in addition, to keep up a sufficient supply

of fresh organic material in the soil, or the use of fertilizers may result in more harm than benefit.

Nitrogen. — The nitrogen is supplied as sodium nitrate or guano (p. 504), calcium nitrate (p. 531), ammonium sulphate (p. 506),

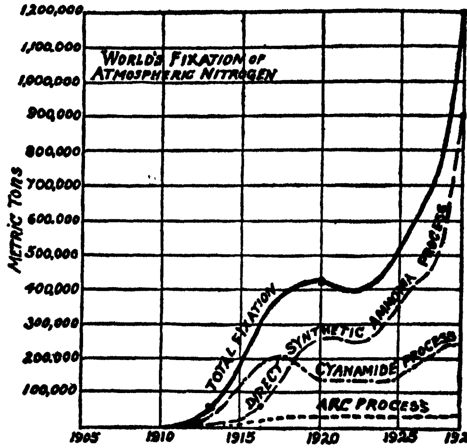


FIG. 177. Development of Nitrogen Fixation Processes.

calcium cyanamide (p. 734), manure or the offal ("tankage") and ground bones from slaughter houses.

The development of nitrogen fixation processes in recent years has been of the greatest importance in connection with the fertilizer industry, as we have already pointed out in the description of these processes (pp. 509, 531). The amounts of atmospheric nitrogen fixed yearly by the various synthetic methods, from 1905 to 1929 inclusive, are shown on the accompanying diagram (Fig. 177). The upward trend of the curves was temporarily disturbed subsequent to 1929 owing to the world depression, but rapid advances are now once more in progress, and the 1935 total approximated 2,000,000 tons.

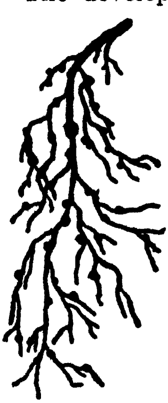


FIG. 178. Root Nodules.

Over every acre of the earth's surface there are 34,000 tons of **free atmospheric nitrogen.** Plants in general are incapable of drawing upon this immense store for the nitrogen necessary for their growth, but peas, beans, clover, alfalfa and other leguminous plants bear round their roots colonies of a special kind of bacteria, which

has the power to bring free nitrogen into combination. In these **root nodules** (Fig. 178) the bacteria first produce proteins, which later decompose, and ultimately yield nitric acid. In this way a crop of clover will fertilize the soil, not only for itself, but also for the following crop. The advantage of rotation of crops is therefore explained.

The beneficial action of bacteria upon plant growth is not limited to this special case. The soil is crowded with bacteria which assist in the decomposition or rotting of vegetable and animal matter. The product, the black, gummy stuff of a fertile soil, is called **humus**. Certain varieties of bacteria convert insoluble carbohydrates such as cellulose into simpler soluble materials, immediately available for plant use. Other species liberate the nitrogen from proteins in the form of *ammonia* and *amino-compounds* (p. 587). Others, again, oxidize these compounds to *nitrous acids* and *nitrites*. Still others, finally, oxidize these products to *nitric acid* and *nitrates*.

The actual assimilation of nitrogen by plants, in whatever form that element is originally present in or added to the soil, takes place almost exclusively through soluble nitrates. The coördinated team-work of all of the above classes of bacteria is therefore an essential point in the efficient utilization of other nitrogen-containing fertilizers.

Phosphorus. — Natural calcium phosphate $Ca_3(PO_4)_2$ is the orthophosphate of calcium. This insoluble salt, however, affords only an exceedingly dilute phosphorus diet for plants. Hence, a more soluble compound is to be preferred. This is found in *calcium acid-phosphate* ("superphosphate") $CaH_4(PO_4)_2$, which is made by heating pulverized natural calcium phosphate with sulphuric acid containing the requisite proportion of water:

$$Ca_3(PO_4)_2 + 2H_2SO_4 + 4H_2O \rightarrow CaH_4(PO_4)_2 + 2(CaSO_4,2H_2O).$$

The whole turns into a dry mixture, consisting of the superphosphate and gypsum (hydrated calcium sulphate). The latter does not interfere with the fertilizing power of the soluble superphosphate, so the mixture is placed directly in sacks and sold as "superphosphate of lime."

In slaughter houses the bones, after being deprived of fat and gelatine, give a residue which is rich in *calcium phosphate*. This residue is treated with sulphuric acid and made into fertilizer.

Potassium. — *Wood ashes* contain much potassium carbonate, and are used as fertilizers for this reason. The giant seaweeds (*kelp*) of the Pacific coast have also been found to contain an unusually large proportion of salts of potassium. By far the most important source of this element, however, is *potassium chloride*, obtained from natural salt deposits.

The average production of the German deposits at Stassfurt in the ten years preceding the war exceeded 1,000,000 tons (calculated as K_2O). These deposits constituted practically a world monopoly, and the shortage of potassium salts for fertilizer purposes during the war was consequently extreme. The most strenuous efforts to develop the potassium resources of the United States (natural brines, kelp, recoverable by-products from the cement and molasses industries, etc.) culminated in a production of barely 50,000 tons of K_2O in 1918. The 1935 production, however, was 193,000 tons, nearly half the annual consumption of 420,000 tons.

Potassium chloride occurs in the Stassfurt deposits as *sylvite* KCl, but is chiefly associated with magnesium chloride as *carnallite* $KCl,MgCl_2,6H_2O$. When water is added to carnallite, a large part of the potassium chloride, which is much less soluble, separates out. Complete extraction and purification of the salt involve a series of recrystallizations. The Alsace deposits contain very little magnesium salts, and the separation of the potassium chloride from the sodium chloride with which it is mixed is comparatively simple.

Potassium sulphate is also obtained from salt deposits, and is substituted for potassium chloride as a fertilizer for certain crops, such as tobacco. Chlorides, in general, melt at lower temperatures than sulphates, and the presence of a chloride in tobacco results in an ash that fuses on burning. This is, obviously, an undesirable property, especially for cigars.

Calcium. — Calcium is naturally present in many soils as *calcium carbonate* $CaCO_3$. In contact with water containing carbonic acid (see p. 567), this gives a solution of the more soluble *bicarbonate* $Ca(HCO_3)_2$. Other compounds of calcium which are used as fertilizers include lime CaO or $Ca(OH)_2$, calcium phosphate and acid phosphate, calcium phosphate or gypsum (p. 728), calcium nitrate and calcium cyanamide.

Manure. — One ton of farm manure contains about 10 pounds of nitrogen (chiefly as urea $CO(NH_2)_2$ and proteins), 5 pounds of phosphoric acid and 10 pounds of potash. The manure is mixed with the soil just before planting seed, or is used as top dressing.

The bacteria in the air and in the soil assist materially in the changes in the manure. Thus urea is hydrolyzed to ammonium carbonate $(NH_4)_2CO_3$:

$$CO(NH_2)_2 + 2H_2O \rightarrow (NH_4)_2CO_3.$$

The proteins are changed by air bacteria into ammonia. The formation of nitrates seldom happens in manure piles, but scattered manure, with the help of soil bacteria, develops nitrates (p. 521).

The potassium compounds form potassium hydrogen carbonate $KHCO_3$. The phosphorus and sulphur compounds become soluble phosphates and sulphates.

Indirect Fertilizers. — Not all substances which are added to the soil are employed with the direct object of their assimilation for plant growth. Often indirect effects induced by their presence are of greater importance. A few cases where calcium salts are of service as indirect fertilizers may be briefly presented as illustrations of this point.

(1) *Gypsum* $CaSO_4,2H_2O$ is added to manure at the rate of 100 pounds per ton. This slightly soluble salt reacts in the soil solution with the ammonium carbonate produced by the hydrolysis of urea, precipitating a much less soluble calcium carbonate and leaving ammonium sulphate in solution:

$$(NH_4)_2CO_3 + CaSO_4 \rightarrow (NH_4)_2SO_4 + CaCO_3 \downarrow.$$

Now ammonium sulphate, being a salt of a *strong* acid with a *weak* base, is only very slightly hydrolyzed in solution (see p. 408). Ammonium carbonate, however, is a salt of a *weak* acid and a *weak* base, and is extensively hydrolyzed. This hydrolysis, unless a large excess of water is present, would lead to rapid loss of ammonia from the manure. The smell of free ammonia, indeed, is often very noticeable in manure piles. The addition of gypsum *fixes* this valuable constituent in the fertilizer for plant use. Lime, on the other hand, would assist in the *liberation* of ammonia.

(2) Gypsum is often added, also, to clay soils with the object of converting insoluble compounds of *potassium* into more soluble compounds. Lime and calcium carbonate are employed to change insoluble *phosphates* of iron and aluminium into more soluble calcium phosphates.

(3) Some soils are either naturally acidic or *sour*, or have become so by excessive use of sulphate fertilizers, and are hence unfavorable to plant growth. This acidity is corrected by addition of lime or calcium carbonate, but *not* gypsum.

(4) Salts which are *injurious* to plants, such as soluble magnesium compounds or "black alkali" (sodium carbonate), are converted into less soluble compounds, such as magnesium hydroxide or carbonate, by addition of lime or calcium carbonate, or into non-poisonous compounds, such as sodium sulphate, by gypsum.

Adsorption in Soils. — As we have seen, fertilizers *must* contain the elements necessary for plant growth in soluble form. It is undesirable, however, to use salts which are exceedingly soluble in water as fertilizers, since they will obviously be rapidly washed away from the surface soil. A large proportion of all fertilizers is unavoidably wasted in this manner. The minute particles of the soil, however, possess the power of conserving dissolved substances

in the soil solution by concentrating and holding them upon their moist surfaces. This phenomenon, *adsorption*, is of considerable interest and importance in other connections, and will be taken up in detail in later chapters (pp. 623, 644, 648).

Exercises. — 1. Given an osmotic pressure cell and an unknown substance, soluble in water, to which the membrane is perfectly impermeable, how could you determine the molecular weight of the substance?

2. What would be the effect of putting fresh flowers in a vase containing a concentrated salt solution?

3. At 20° 100 c.c. of water, shaken up with excess NaCl and KCl, dissolve 30 g. NaCl and 15 g. KCl. At 100° the same amount of water, in equilibrium with the same two solids, contains 20 g. NaCl and 40 g. KCl. On the basis of these figures, devise a method for separating KCl from NaCl in the Alsace deposits.

4. The use of ammonium sulphate as a fertilizer is apt to result in an *acid soil.* Explain why.

5. What are the four elements most needed in fertilizers? Of which does every country have a free and unlimited supply? How can it be made available?

6. What valuable soil ingredients are lost to a locality when a carload of wheat is shipped away? A carload of pure sugar? Of cotton, (*a*) ginned or (*b*) unginned? Of cotton-seed oil (p. 633)?

7. Plot osmotic pressure against concentration for a solution of cane-sugar from the following data at 0°:

G. mols. sugar per liter sol'n.						
0.095	0.263	0.517	0.750	1.581	1.929	2.197
Osmotic pressure, atmos.						
2.23	6.85	14.21	21.87	67.74	100.13	134.84

Plot, on the same diagram, the osmotic pressure values for the same solutions calculated from the gas laws. [Assume, in other words, that a solution containing 1 g. mol. of sugar per liter would exhibit an osmotic pressure of 22.4 atmospheres at 0°. Draw a straight line from the point so obtained on your diagram to the origin.] Does the observed curve correspond with the calculated? What is your conclusion?

8. 300 c.c. of commercial "water glass" (p. 661) is diluted with an equal volume of water, and the solution is divided among six small beakers. Into the first beaker a few crystals of copper sulphate are dropped, into the second a few crystals of nickel sulphate, into the third cobalt chloride, into the fourth ferric chloride, into the fifth lead nitrate, into the sixth chrome-alum (p. 881). What do you observe? Explain on the basis of semi-permeable membranes and osmotic pressure.

9. If a crop of wheat removes 41 pounds of nitrogen per acre (p. 611), what weights of the following fertilizers would theoretically satisfy nitrogen requirements for a field of 100 acres: (*a*) sodium nitrate, (*b*) calcium nitrate, (*c*) ammonium sulphate, (*d*) calcium cyanamide?

10. In practice, would the amounts calculated in the preceding exercise really be sufficient? If not, why not?

11. What weight of phosphorus is contained in 1 kg. of "superphosphate of lime" (p. 613), 90 per cent pure?

12. What is the percentage of potassium in carnallite? Mention as many reasons as you can why carnallite itself is not used as a fertilizer.

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CHAPTER XXXVI

PLANT PRODUCTS. FERMENTATION AND FUELS

Having described the chemistry of plant life and growth, we may now proceed to the chemistry of substances resulting therefrom. Foods will be taken up separately in the following chapter. In the present chapter we shall restrict ourselves to two other main branches, **fermentation products** and **fuels.**

Enzymes. — All fermentations are brought about either directly or indirectly by the activities of animal or vegetable organisms. The most familiar ferment, of course, is **yeast.**

Yeast belongs to a low order of plants and consists of minute cells. Its value lies in the fact that, while growing and multiplying, it secretes within each cell small amounts of two very active chemical substances which are dissolved in the cell contents. These substances are known as **zymase** and **invertase** (or **sucrase**), and belong to the class of organic materials called **enzymes.** Enzymes produce remarkable chemical changes in organic materials by their mere presence (contact actions). These changes are *specific,* each enzyme acting only on certain carbohydrates, for example, and being quite inert towards others.

Fermentation of Sugars. — When a cake of yeast is broken into an aqueous solution of glucose or grape-sugar (p. 602), the small amount of zymase present causes the gradual decomposition of the sugar. The most favorable temperature is about 30°. Bubbles of carbon dioxide soon begin to rise to the surface, and the gas can be led off (Fig. 179) to exhibit its characteristic action (p. 567) on lime-water. At the same time **ethyl alcohol** C_2H_5OH accumulates in the liquid as the sugar disappears:

$$C_6H_{12}O_6 \rightarrow 2CO_2 \uparrow + 2C_2H_5OH.$$

The liquid extracted from the yeast cells works as well as does the plant itself.

Yeast will ferment fructose (fruit sugar, p. 603), with the same result, but more slowly.

Zymase does not act upon cane-sugar (sucrose $C_{12}H_{22}O_{11}$). But the invertase (sucrase), which is also contained in the yeast, hydrolyzes the sucrose in the same way as does a dilute acid, giving invert sugar (p. 604). The latter is then decomposed by the zymase. Hence cane-sugar in solution is decomposed by yeast into alcohol and carbon dioxide, just as is grape-sugar, only less rapidly.

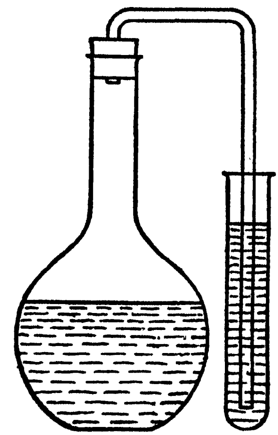


FIG. 179. Fermentation of Sugar.

In the manufacture of **wines** the glucose contained in the grape juice is fermented by a species of yeast always found on the skins.

Fermentation of Starch. — Barley, which has been allowed to sprout, and is then dried, is called **malt.** This contains an enzyme, **diastase** (or **amylase**), which is able to hydrolyze starch into maltose $C_{12}H_{22}O_{11}$ (p. 603). Maltose is further hydrolyzed by another enzyme, **maltase,** to form glucose, and the latter is then decomposed by zymase into alcohol and carbon dioxide.

Whiskey is made by treating the starch of rye, maize, or barley in the above way, with subsequent distillation. **Beer** is made similarly from various kinds of grain, particularly barley, except that the fermented liquid is not distilled.

Distillation of Ethyl Alcohol. — Mixtures of two liquids, when distilled, behave in one of three ways. Two of these have been described already (pp. 228, 579), and **alcohol** (b.-p. 78.30°) and **water** (b.-p. 100°) illustrate the third. In this case the vapor tension of a certain mixture is *higher* than that of any other mixture and higher than that of either component separately. This special mixture has, therefore, a *lower* boiling-point than any other. In the present instance this mixture contains 95.57 per cent of alcohol and 4.43 per cent of water and boils at 78.15°. When the fermented liquid, with its large percentage of water, is distilled, the alcohol all tends to pass off first, in association with that part of the water required to constitute the mixture of minimum boiling-point. Re-

peated distillation simply eliminates more completely the excess of water beyond this amount (*viz.*, 4.43 per cent), by leaving it in the residues.

Absolute alcohol, which boils at 78.3°, cannot be made by distillation alone. It is prepared by adding quicklime, which combines with the water, and redistilling the liquid.

Industrial Alcohol. — Alcohol has very extensive uses, apart from its historic importance as a beverage. It is employed as a *solvent* in making varnishes for wood and lacquers for metal, as well as for plastics like celluloid, collodion and artificial silk (p. 652). It is of service in the *purification* of many natural organic products, such as *turpentine,* and in the *preparation* of many synthetic organic products, such as *dyes.* It is also rapidly coming into use as a *fuel,* its smokeless flame and efficiency of combustion making it of special importance for aeroplane and motor engines. *Solidified alcohol,* obtained by the addition of cellulose esters (p. 652), is now largely employed for *cooking* purposes. Another new development is the catalytic production of ethylene for *cutting and welding* (p. 586). As an *anti-freeze* for automobile radiators, alcohol has now been largely displaced by glycerine and other organic liquids, which do not boil away so readily.

Alcohol, as used in the industries, is *denatured,* or rendered unsuitable for drinking purposes, by addition of small quantities of benzine (p. 578), pyridine bases, or other disagreeable and nonremovable organic liquids. The exact formula of denatured alcohol depends upon the use for which it is intended.

The cheap production of industrial alcohol is rendered possible by the utilization of certain waste materials rich in carbohydrates. When the price of food is high, *grains* are employed in the manufacture of alcohol only when a crop has been damaged in some manner so that it cannot be sold as a food material. When *sawdust* or *wood refuse* is heated with dilute sulphuric acid under pressure, the cellulose is converted into fermentable sugars by hydrolysis (compare p. 604). At the present time, however, the most important source of industrial alcohol in the United States is *molasses.* Only a few years ago the disposal of molasses furnished a very troublesome problem to the sugar mills, but in 1935 nearly 200,000,000 gallons of molasses were used in the production of industrial alcohol in the United States alone.

Synthetic methods for producing alcohol have recently been devised which will undoubtedly play an important part in the industrial development of the future. Thus, for example, acetylene C_2H_2, obtained by the action of water on calcium carbide, is converted by a catalytic process of hydration to acetaldehyde $CH_3.CHO$ (p. 582). This conversion is most readily carried out by leading acetylene into a hot concentrated solution of sulphuric acid or phos-

phoric acid (the catalyst), containing a dissolved mercury salt, which functions as a promoter (p. 570):

$$C_2H_2 + H_2O \rightarrow CH_3.CHO.$$

The next stage consists in the hydrogenation of the acetaldehyde to ethyl alcohol. This is effected by leading a mixture of hydrogen and acetaldehyde vapor over a suitable catalyst, for instance finely-divided nickel (compare p. 634):

$$CH_3.CHO + H_2 \rightarrow C_2H_5OH.$$

Other alcohols may be manufactured by similar methods. A most interesting and valuable new process for the production of methyl alcohol (methanol) CH_3OH consists in passing a mixture of hydrogen and carbon monoxide, in the proportions by volume of at least two to one, over a catalyst composed chiefly of zinc oxide, with other oxides present as promoters:

$$CO + 2H_2 \rightarrow CH_3OH.$$

Acetic Acid CH_3COOH. — This acid is formed by the partial oxidation of alcohol (p. 583). **Vinegar** (crude acetic acid) is manufactured by oxidizing alcohol with atmospheric oxygen, using a bacterium (*Bacterium aceti*, "mother of vinegar"), or more probably an enzyme which it secretes, as a contact agent. The dilute alcohol, in the form, for example, of "hard" cider (fermented apple juice), is allowed to trickle over shavings in a barrel. The shavings are inoculated with the *Bacterium aceti* by preliminary wetting with vinegar. Holes in the sides permit a plentiful supply of air, to the action of the oxygen of which the liquid is exposed by being spread over the surface of the shavings:

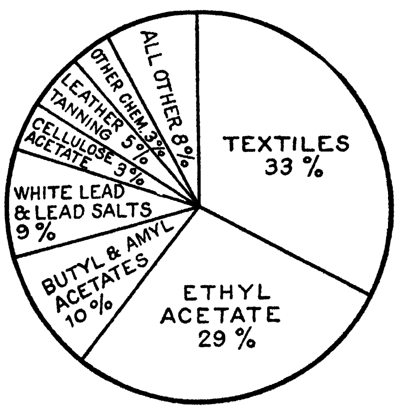


FIG. 180. Distribution of Acetic Acid in Industry.

$$C_2H_5OH + O_2 \rightarrow CH_3.COOH + H_2O.$$

The liquid (vinegar), which issues at the bottom, contains from 5 to 15 per cent of acetic acid, besides coloring and flavoring matters derived from the fruit juices.

Pure acetic acid may be prepared by distilling the vinegar repeatedly. It is derived more cheaply, however, from the liquid

distillate obtained by heating wood in the manufacture of charcoal. Large quantities are used (Fig. 180) in the textile industries, in the preparation of white lead (p. 833), and in the manufacture of various synthetic organic products (see, for example, p. 651).

Pure (or glacial) acetic acid is a colorless liquid, which boils at 118° and freezes at 16.7°. Although four atoms of hydrogen are contained in its molecule, only one of these is replaceable by metals. This fact is recognized in its reaction formula $CH_3.COOH$ (p. 583). It is a weak, monobasic acid:

$$CH_3.COOH \rightleftarrows H^+ + CH_3.COO^-.$$

Acetic acid is also manufactured now in large quantities by a synthetic process, namely by the oxidation of acetaldehyde, obtained as described on p. 621. Atmospheric air or oxygen is used as the oxidizing agent, and various metallic salts such as manganous acetate are employed as catalysts:

$$2CH_3CHO + O_2 \rightarrow 2CH_3.COOH.$$

Fuels

Destructive Distillation of Wood. — When dry wood is heated in iron retorts in absence of air, the compounds which it contains are decomposed. Much of the carbon remains in the form of **charcoal.** The vapors which pass off deposit, when cooled, much **liquid material.** The uncondensed **gases** are combustible and are used for heating the retorts or other similar purposes. Hard wood furnishes, approximately, 25 per cent of its weight of charcoal, 25 per cent of gases, and 50 per cent of liquids. The liquid contains acetic acid (10 per cent), methyl alcohol CH_3OH or wood spirit (3 per cent), a complex tarry mixture used in road-making (10 per cent), water (77 per cent), and a little acetone (p. 583). The distillate from resinous wood also contains valuable quantities of *turpentine*, $C_{10}H_{16}$, an unsaturated hydrocarbon used extensively as a solvent. The gases evolved contain a large part of the nitrogen of the original proteins in the form of ammonia, which is dissolved out with water.

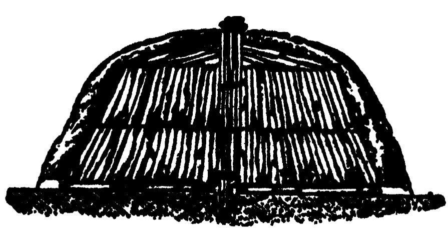


Fig. 181. Charcoal Pile.

When charcoal only is desired, the wood is stacked, covered with turf (Fig. 181), and set on fire. A part is burned, the rest is converted into charcoal, and all the valuable volatile products are lost.

Properties of Wood Charcoal. Adsorption. — The charcoal retains the structure — a complex network of minute cells — of the original wood, and therefore has a *surface* which is vast in proportion to the amount of material it contains. Upon this surface it is capable of taking up or *adsorbing* many times its own volume of gases, especially of the more condensible ones. Thus, boxwood charcoal takes up ammonia (90 volumes), hydrogen sulphide (55 volumes), and oxygen (9 volumes).

The adsorption is exceedingly rapid and, in the case of a condensible gas contained in small quantity in air, practically complete. For this reason, charcoal and other substances with very finely divided surfaces are used as adsorbent materials for industrial gases and vapors (compare silica gel, p. 662), and also as catalysts for many gaseous reactions (see pp. 419, 507).

The **toxic gases** employed in the Great War are also readily adsorbed by charcoal. Hence the canisters of gas masks contain layers of porous charcoal, together with granulated soda-lime and potassium permanganate, which react *chemically* with certain of the noxious gases liable to be present. During the war vast strides were made in increasing the adsorptive power of various kinds of charcoal by modifications in methods of carbonization, the most efficient of all charcoals being dense varieties derived from *cocoanut shells* and *fruit pits*. Canisters packed with such charcoal reduced the concentration of all toxic gases employed in the war (see Chapter XXXVIII) below the danger limit. Toxic *smokes*, however, were not satisfactorily adsorbed. The explanation is similar to that advanced in a preceding chapter (p. 421) for the persistence of the fog obtained when a mixture of sulphur trioxide and oxygen is bubbled through water. The molecules of a gas are in such rapid motion that they are practically certain to strike the surface of the charcoal while passing through the canister, and to be adsorbed on this surface if the gas is easily condensible. The dimensions of the solid smoke particles, however, are much larger than molecular, and the particles are relatively stationary. Most of them, in consequence, are able to pass through the air channels between the charcoal granules without touching.

Pulverized charcoal, when shaken with a liquid, is also able to extract from it any dissolved substances, and to concentrate them

upon its surface. Other finely divided materials, such as soil particles (p. 615), possess the same power of adsorbing substances from solution. Salts are, in general, only partially taken up; organic solutes are removed more completely. This property of charcoal is made use of in **water purification** and in **sugar refining** (p. 603). Charcoal is used, also, in making gunpowder, in reducing ores, and as a fuel (smokeless).

Coal. —When wood burns with a plentiful supply of oxygen, it gives nothing but carbon dioxide, water, free nitrogen, and a certain amount of ash (oxides and carbonates of the metals). What happens when it is heated in absence of oxygen, we have just seen. In nature, however, the intermediate case of slow decomposition of vegetable matter, *without* much heating and *without* access of

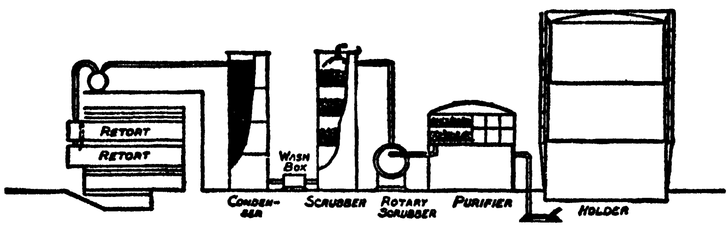


FIG. 182. Manufacture of Coal Gas.

oxygen, takes place on a large scale. Clay and sand, or even simply water, cover the vegetation and exclude the air, and the products are anthracite coal, bituminous coal, or peat. Little is known of the actual compounds contained in coal. We are concerned mainly with the products obtained by heating it in the absence of air, and with its use as a fuel.

Bituminous coals give much, and widely varying amounts, of volatile matter; anthracite coals give very little. The ash is the mineral matter of the original plants, with additional rock materials in some specimens. The coal is selected according to the purpose for which it is to be used. For coal gas, and even for coke, a variety high in volatile matter is chosen. For water gas (p. 569), anthracite or coke itself is employed.

Coal Gas. —The gas plant (Fig. 182) includes (1) the fire-brick retorts in which the coal is heated (externally) to 1300°, (2) the hydraulic main (a wide iron pipe) immediately above them in which most of the tar collects, (3) the condenser and wash box for cooling, condensing, and removing oils, (4) the scrubbers (verti-

cal and rotary) where the ammonia is taken out by water dripping over strips of wood and by stirring the gas with water, (5) the purifier where hydrogen sulphide is taken up by hydrated ferric oxide, and (6) the holder in which the gas collects.

The yield of gas varies considerably with the type of coal used. One ton of good *bituminous coal* should produce approximately 10,000 cubic feet of coal gas, 1300 pounds of coke, 5 pounds of ammonia and 12 gallons of tar. The average composition of coal gas is: Illuminants 4 per cent, carbon monoxide 8 per cent, hydrogen 50 per cent, methane 29 per cent, ethane 3 per cent, carbon dioxide 2 per cent, oxygen and nitrogen 4 per cent.

The ammonia is made into ammonium sulphate. The tar may be used for road-making, as a waterproof material in building, and wherever pitch is applicable. More frequently it is separated by distillation, and other forms of treatment, and yields benzene C_6H_6, naphthalene $C_{10}H_8$, anthracene $C_{14}H_{10}$, phenol or carbolic acid C_6H_5OH and innumerable other valuable substances.

Coke Ovens. — The **by-product coke oven** is very much like the plant used for making coal gas. The difference is that the heating is arranged so as to decompose the volatile matter and cause it to leave as much as possible of its carbon behind. The resulting gas is consequently poor in illuminants, but excellent as a fuel. The ammonia and tar are also diminished in amount, but are still produced in paying quantities.

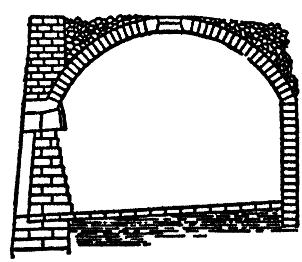


FIG. 183. Beehive Coke Oven.

The **beehive coke oven** (Fig. 183), now largely discarded, is a primitive device of fire-brick, shaped like a beehive. It is simply filled with coal, part of which is allowed to burn with a limited supply of air. It yields 66 per cent coke, against 73 per cent from the by-product oven. All the volatile matter, with its gas, ammonia, and tar, escapes through an opening at the top, where it burns in a large flame and is wasted.

Coke is a gray-black, hard material of spongy texture. It burns without flame, and gives a higher temperature than does coal, because no heat is used in vaporizing moisture and volatile matter. On account of these and other properties, it is used in immense quantities in reducing ores of iron and other metals, and in smaller amounts in electric furnace work.

Recently, much attention has been attracted to the question of the *low-temperature carbonization* of coal, since below 600° far larger quantities of liquid fuels are obtainable than in high-temperature coking. Certain rich grades of coal can be made to yield as high as thirty gallons of tar and motor spirit per ton. Considerably greater amounts than this, however, can be obtained from bituminous coal or from lignite (brown coal) by the **Bergius liquefaction process.** The coal, ground to a fine powder, is made into a paste with cheap, heavy oil and treated with hydrogen at 420–450° under a pressure of 200 atmospheres. The consequent hydrogenation (compare p. 634) gives a liquid product which is decomposed, by cracking, into gas, valuable oils of low boiling-point, and pitch.

Coal as Fuel. — The quality of a fuel coal, and whether it is worth its price, is learned by measuring its **calorific** (heating) **power.** A sample (about 1 g.) is burned in a **bomb calorimeter.** This is a closed, metal vessel, filled with oxygen and submerged in a known weight of water. The coal is set on fire by a wire heated electrically and, after it has burned, the increase in temperature of the water is read off. Hence the heat in calories (p. 257) evolved by the burning of 1 g. of coal is obtained. In engineering practice they use the number of British Thermal Units (1 B.T.U. = heat required to raise 1 pound of water 1° F.) developed by 1 pound of coal, and call the result the calorific power. Since 1° C. = 1.8° F., the number of British Thermal Units is evidently equal to 1.8 times the number of calories per gram of coal.

	Calories per 1 g.	B.T.U. per 1 lb.		Calories per 1 g.	B.T.U. per 1 lb.
Hydrogen	28,800	51,840	Bituminous coal	7,800	14,040
Charcoal (to CO_2)	8,080	14,544	Anthracite	8,000	14,400
Wood (seasoned)	4,750	8,550	Petroleum	11,000	19,800

Knowing that 100 cal. will raise 1 g. of water from 0° C. to 100° C., and 540 cal. more will convert it into steam, it is possible to calculate how much steam should be furnished by 100 kg. of coal of known heat of combustion. If the quantity falls short, then the furnace, draft, or method of firing may be defective. Too much draft, for example, merely introduces additional, useless air to be heated. Thus, if the flue gas, upon analysis, is found to contain, not 12 per cent carbon dioxide (normal), but only 3 per cent, then for every ton of coal burned, 52 tons of unnecessary air have been raised to the temperature of the furnace. By chemical tests, made in ways like this, the efficiency of every device in the modern factory is (or ought to be) controlled. If the coal is bought without heed to its calorific value, and used without experimental checks, the boiler house alone may easily waste the whole profit earned by the rest of the plant.

Source of the World's Energy. — The energy that does the world's work comes mainly from two sources, namely, water power and the combustion of wood or of coal (which is fossil wood). The water comes from vapor, generated by the *sun's heat,* condensed as rain, and collected in lakes or reservoirs. The source of the energy of coal or wood is a little less obvious. When wood (which is largely cellulose) burns, it gives carbon dioxide, water, and heat. In fact, its combustion is represented by the equation on p. 598, *when this equation is read backwards.* Thus the sunlight, working through the machinery of the plant, takes the carbon dioxide and water, furnishes the energy (as light), and gives us wood and oxygen. And the wood and oxygen, when burned, give us back the original substances, and the equivalent of the original energy in the form of heat. Hence, our other main source of energy turns out to be the same as the first — the sun's rays — although the route by which the energy comes to us is a little less direct.

If, instead of *burning* the starch of the plant, *we consume it as food,* it goes through a *series* of changes instead of only *one.* But the end products are the same, namely, carbon dioxide and moisture issuing from our lungs, and heat and other forms of energy such as are developed in living organisms. Thus, whether we use our muscles, a steam engine, or a waterwheel to do work, sunlight is in each case the ultimate source of energy employed.

It should be noted that the energy is not stored exclusively in the fuel we burn, or in the food we eat, but is shared between these materials and the oxygen of the air. If our atmosphere consisted of compounds of carbon, then the material corresponding to stores of coal would have to be oxygen or compounds of oxygen, and we should be likely then to speak of the energy as being stored for us and sold in the form of oxygen. That we are in the habit of speaking of it, at present, as going with the other materials is because the oxygen of the air is supplied free of charge, while coal and food have to be purchased.

Exercises. — 1. In fermentation, why does not carbon dioxide appear in bubbles *at once?*

2. How do we ascertain that acetic acid in aqueous solution is only slightly ionized? Give as many methods as possible.

3. (*a*) Why are charcoal and coke smokeless fuels? (*b*) Explain why bituminous coal burns with flames while anthracite does not.

4. Point out the analogies between the processes used in making coke and charcoal, and between their properties and uses.

5. A gas of sp. gr. 0.43 (air = 1) gives, on burning, 610 B.T.U. per cu. ft. at 0°. How many B.T.U. is this per pound?

6. How many kg. of steam, from water at 20°, can be made by burning 100 kg. of coal, the heat of combustion of 1 g. of which is 8500 cal.?

7. What is "conservation"? What four industries or operations (or ways of performing operations) that are *wasteful* have been mentioned in this chapter (compare p. 506)?

8. Correlate the industrial uses of alcohol with its physical and chemical properties.

9. What is the normality of a sample of acetic acid, of density 1.007, containing 5 per cent by weight of the pure acid? How many c.c. of 0.5 *N* sodium hydroxide would be required to neutralize 100 c.c. of the sample?

10. Would a gas mask packed with charcoal be efficient in an atmosphere contaminated with carbon monoxide? What could be used instead (p. 572)?

11. What compounds contained in the original plants furnish the hydrogen sulphide and the ammonia obtained on distilling coal?

12. When an anti-freeze material is added to the water in the radiator of an automobile in winter, what principle is being applied? What properties are essential for an *anti-freeze?*

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CHAPTER XXXVII

ANIMAL LIFE AND ANIMAL PRODUCTS. FOODS

Only a few of the more important points in the chemistry of animal life and growth can be touched upon here. In the same way, the chemistry of **foods** is presented merely in outline. Some food products, derived from plants, have been described in earlier chapters. The single animal product dealt with in any detail in the present chapter is **soap.** In connection with soap, the subject of **colloids** is also briefly discussed.

Colloid chemistry is a subject of great fascination, with a great many industrial applications. It is, however, a highly dangerous field for the beginning student, since is it so easy to misinterpret what you are told and to depart from a rapid survey with nothing more than a colloidal state of mind. For this reason we have not tried to cover the topic systematically in this chapter. The average teacher with the average class will find it preferable to postpone detailed work on the subject to a subsequent course, where more opportunity is afforded for practical work and mathematical discussion.

The exceptional instructor, however, may wish to give his students a little extra information on colloids at this stage, and the exceptional student may wish very much to obtain such information. Reference should be made, in such cases, to one of the following texts:

Hatschek, *An Introduction to the Physics and Chemistry of Colloids* (Blakiston's Sons and Co.).

Bancroft, *Applied Colloid Chemistry* (McGraw-Hill Book Co.).

Thomas, *Colloid Chemistry* (McGraw-Hill Book Co.).

Hedges, *Colloids* (Arnold & Co.).

Composition of the Human Body. — The following gives, roughly, the percentage of each element in the human body.

O	65	N	3	K	0.35	Cl	0.15	I	trace
C	18	Ca	2	S	0.25	Mg	0.05	F	trace
H	10	P	1	Na	0.15	Fe	0.004	Si	trace

We have already learned that the calcium and phosphorus are chiefly in the bones (p. 541). The nitrogen, sulphur, and iron are in the proteins. The sodium is largely present as salts, in the fluids

of the body. The potassium is in the soft tissues and in special secretions like milk. As in the plant, the carbon, hydrogen, and oxygen are in the form of carbohydrates, proteins, and fats, and there is also much water.

Certain amounts of all these elements leave the system daily. Water evaporates from the lungs and skin. The carbon leaves in large amounts, chiefly from the lungs as carbon dioxide, and also as excreted fats, proteins and carbohydrates. Much of the nitrogen is eliminated in the urine, chiefly as urea $CO(NH_2)_2$. The salts are removed in the same way.

Animal Nutrition. — Since there is continual loss, there must be continual replacement. The animal resembles the plant in the fact that it can take up into its system *only dissolved material.* It differs from the plant, however, in the fact that it is provided with a wonderful laboratory in which insoluble substances are changed into soluble ones. This is the *digestive tract,* consisting of the mouth, stomach, and intestine. The production of soluble substances of suitable composition is called *digestion.*

The *processes* are too complex for detailed treatment here. Only a few typical *illustrations* can be given. The *principles* concerned have all been used and illustrated already, and many of the facts are contained in previous chapters.

Foods. — First, let us examine the accompanying table, showing the percentage composition of the edible portion of several articles

Food Material	Water	Protein	Fat	Carbo-hydrate	Ash
Beef (lean)	73.8	22.1	2.9	.....	1.2
Cod	82.6	15.8	0.4	.....	1.2
Eggs	73.7	14.8	10.5	.....	1.0
Milk*	87.0	3.3	4.0	5.0	0.7
Butter	11.0	1.0	85.0	.....	3.0
Cheese (cheddar)	27.4	27.7	36.8	4.1	4.0
Oatmeal	7.3	16.1	7.2	67.5	1.9
Wheat flour	11.9	13.3	1.5	72.7	0.6
Beans (dried)	12.6	22.5	1.8	59.6	3.5
Almonds	4.8	21.0	54.9	17.3	2.0
Maize (green corn)	75.4	3.1	1.1	19.7	0.7
Potatoes	78.3	2.2	0.1	18.4	1.0
Lettuce	94.7	1.2	0.3	2.9	0.9
Sugar	....	....	....	100.0	...

* The emulsified fat separates slowly as the cream; the protein (casein, colloidally suspended in the skim milk) is coagulated by rennet and constitutes cheese; the carbohydrates (lactose, a sugar) are then left in the water, along with inorganic salts.

of food. We note, at once, that there is little more water in milk than in cod; that the animal foods, except milk, contain no carbohydrates; that potatoes and corn when dried are nearly all carbohydrates (starch); that lean beef when dry is nearly all protein; that some seeds (wheat and beans) contain almost no fat, some (oats) much more, and some (almonds and nuts) a very large amount; and that lettuce and other leaves are mainly water, with dissolved inorganic salts (valuable), contained in a light framework of cellulose (non-digestible).

Digestion of Starch. — The carbohydrates, in most foods which contain a large proportion of them, are mainly in the form of starch. The exceptions are milk, sweet fruits, and sugar itself. Starch is insoluble in water, and cannot be directly absorbed. But we have seen (p. 602) that, when boiled with a dilute acid, it is hydrolyzed, giving glucose. When bread and potatoes are masticated, an enzyme (p. 618), named **ptyalin,** contained in the saliva (alkaline), turns a part of it, by hydrolysis, into a soluble sugar, maltose. Later, in the small intestine, **amylopsin** completes this process. Here also another enzyme, **maltase,** splits the maltose into glucose. The glucose then passes through the intestinal wall and so goes into the circulation, where most of it is oxidized.

The *cooking* of starch (*baked* bread, *boiled* potatoes, etc.) breaks up the grains and makes the mixing with the enzyme more perfect and the digestion more rapid and complete.

Baking Powders. — The purpose of the powder is to generate carbon dioxide in the dough. The bubbles of the gas are retained by the sticky gluten of the flour. They expand when the dough is baked, and give to it the open texture which, when the bread is eaten, facilitates access of the saliva to every particle.

Baking soda $NaHCO_3$, if used alone, will give off, when heated, half the carbon dioxide it contains (p. 418). The sodium carbonate which remains in the bread, however, has an acrid taste. By its action on the gluten in the flour, it gives also a yellow color and an unpleasant odor. Finally, the carbonate of soda tends to neutralize the gastric juice (acid) of the stomach and so to interfere with digestion.

To obviate these difficulties sour milk (containing lactic acid) is sometimes used in making the dough. Occasionally vinegar (p. 621) is added. Most frequently a baking powder, containing an acid substance along with the soda, is employed. Typical acid sub-

stances contained in baking powders are anhydrous sodium aluminium sulphate, acid-phosphate of calcium or sodium, and potassium-hydrogen tartrate. The last, known commonly as **cream of tartar** $HKC_4H_4O_6$, acts as follows:

$$HKC_4H_4O_6 + NaHCO_3 \rightarrow NaKC_4H_4O_6 + H_2O \uparrow + CO_2 \uparrow .$$

The sodium-potassium tartrate which remains is better known under the name of *Rochelle Salt.*

It is important that the soda and the acid substance should be used *in the correct proportions,* which can be calculated from the equation. In commercial baking powders a little corn-starch is added, to keep the particles of the other compounds apart and prevent that gradual interaction which otherwise would be bound to occur. The acid substance should also be somewhat insoluble, so that, even when wet, it will not act upon the soda until ample time has been allowed for complete mixing with the dough.

The "raising" of baker's bread is effected by adding yeast. The batch is "set" in a warm place for some hours to permit the yeast to propagate and to act upon the sugar in the flour. In this action, as we have seen (p. 618), carbon dioxide and alcohol are produced. A little sugar, molasses, or malt extract is added to the dough, to afford a larger supply of the sugar required for the production of the carbon dioxide.

The whites of eggs "raise" cake, without the presence of any soda, because of the expansion under heat of the bubbles of air entangled with the albumen when the eggs are "whipped."

Fats and Oils. — The fats and oils found in the bodies of animals, or pressed from the seeds of plants, are composed mainly of various esters (p. 583). As such, they are formed by the interaction of a tribasic alcohol, **glycerine** $C_3H_5(OH)_3$, with higher acids of the paraffin and olefine series of hydrocarbons, such as the saturated acids $C_{15}H_{31}.COOH$ **(palmitic acid)** and $C_{17}H_{35}.COOH$ **(stearic acid),** and the unsaturated acid $C_{17}H_{33}.COOH$ **(oleic acid).** For example:

$$\underset{\text{glycerine}}{C_3H_5(OH)_3} + \underset{\text{palmitic acid}}{3H(COO.C_{15}H_{31})} \rightleftarrows \underset{\text{glyceryl palmitate}}{C_3H_5(COO.C_{15}H_{31})_3} + 3H_2O.$$

The glycerine esters of the saturated acids are solid at ordinary temperatures (fats), while those of the unsaturated acids are liquid (oils). **Beef suet** is a mixture of about three-fourths glyceryl palmitate (palmitin) $C_3H_5(CO_2C_{15}H_{31})_3$ and glyceryl stearate (stearin) $C_3H_5(CO_2C_{17}H_{35})_3$, and one-fourth glyceryl oleate (olein) $C_3H_5(CO_2C_{17}H_{33})_3$. **Hog lard** contains about 40 per cent of the former and 60 per cent of the latter, and is therefore softer. **Butter**

includes the same esters, with about 14 per cent of water and 7 per cent of glyceryl butyrate (butyrin) $C_3H_5(CO_2C_3H_7)_3$. **Olive oil** contains 75 per cent of olein. **Cotton-seed oil** (see p. 634) is similar in nature.

All these fats and oils contain, also, a small amount of the *free acids*. They must not be confused with *mineral oils* like petroleum, which are mixtures of hydrocarbons.

Oleomargarine is an artificial butter. It is made by straining melted beef fat and allowing it to stand at 24°. Much of the stearin crystallizes out and the remaining liquid (the "oleomargarine") is pressed out and allowed to harden. The solid is finally mixed with a little of some oil, to render it softer, and is churned with milk to impart the proper flavor. Although it lacks the butyrin, the product is similar in chemical nature to butter, and is just as nutritious and wholesome (see, however, Vitamins, pp. 636–8).

Hydrolysis of Fats and Oils. — The chief chemical property of the fats and oils, and in fact of all esters, is that each can be *decomposed*, or hydrolyzed, to give back the alcohol and acid from which it is derived. Thus, when ethyl acetate is boiled with water, it is slowly decomposed into ethyl alcohol and acetic acid:

$$C_2H_5(CO_2CH_3) + H_2O \rightarrow C_2H_5OH + HCO_2CH_3.$$

In the case of the fats and oils, if water alone is used, they must be heated in a closed vessel, or autoclave, under pressure so as to secure a high temperature (about 200°):

$$\underset{\text{palmitin}}{C_3H_5(CO_2C_{15}H_{31})_3} + 3H_2O \rightarrow \underset{\text{glycerine}}{C_3H_5(OH)_3} + \underset{\text{palmitic acid}}{3HCO_2C_{15}H_{31}}.$$

When the mixture has cooled, the acid, which is insoluble in water, forms a solid cake, while the glycerine is dissolved in the water.

With water alone as a hydrolyzing agent, however, the reaction is slow and incomplete and, at the high temperatures which it is necessary to employ, some destruction of fatty matter is apt to occur. In the presence of dilute sulphuric acid as a catalyst, the hydrolysis can be carried out much more satisfactorily and rapidly, even at 100°. Sulpho-derivatives of the fatty acids are still more effective as catalysts, since they are freely soluble both in fats and oils and in water, and hence promote the miscibility of the two layers (**Twitchell process**).

When tallow (beef fat) is treated in this way, the product is a mixture of palmitic, stearic, and oleic acids. The latter, being liquid, is pressed out, and the solid material is used with paraffin in

making candles. The glycerine is separated from the water and used in making nitroglycerine (p. 652), as an anti-freeze (p. 620), and in medicine.

Hydrogenation of Oils. — The market value of solid fats is much higher than that of liquid oils. Many natural oils, indeed, possess disagreeable characteristics (taste, odor, etc.) which render them totally unsuitable for edible purposes. They may be converted into more appetizing edible fats, however, by *hydrogenation.* At 200°, in the presence of finely divided nickel as a catalyst, these unsaturated compounds take up hydrogen and become saturated, the oil *hardening* to a fat in the process.

Many substances which were formerly waste products, such as cotton-seed oil, are now treated in enormous quantities in this way (see Fig. 184). The hydrogenation of low grade oils (for example, fish oil) is also of great industrial importance in the manufacture of **soap** (see p. 639) and **candles.**

Digestion of Fats. — At body temperature, the fats and oils present in foods are all insoluble in water, and therefore cannot be directly absorbed into the system. But fats, if already emulsified (p. 198), as in milk, are hydrolyzed by a **lipase** (enzyme for *fat*) in the gastric juice of the stomach, and are decomposed into the acid and glycerine (p. 633). Fat in larger masses is hydrolyzed by lipases in the bile and here the acid (insoluble in water) is dissolved. The acid and the glycerine then diffuse through the intestinal wall and finally recombine to form fat in the blood. Some of this fat is deposited in the tissues and some is oxidized (giving muscular energy and heat).

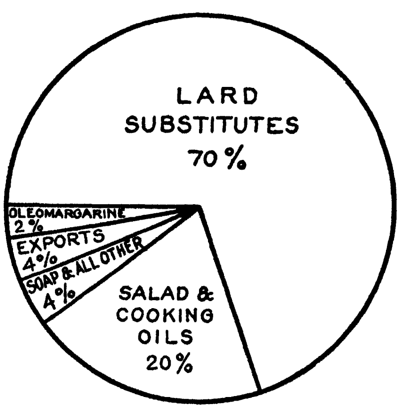


FIG. 184. Distribution of Cotton-seed Oil in Industry.

Cooking (application of heat) does not affect the digestibility of fat. However, when fat is heated too strongly, the beginning of destructive distillation produces unsaturated compounds. These are intensely irritating to the digestive organs — as the way their vapors bring tears to the eyes would lead us to expect.

Digestion of Proteins. — The proteins contained in foods, of which the white of an egg (albumen) is a typical example, are not affected by saliva, but, when mixed with the gastric juice of the stomach, they are changed by the free hydrochloric acid it contains into **syntonin.** This in turn is hydrolyzed by the **pepsin** (enzyme), also contained in the gastric juice, into **peptones** which are soluble in water. These changes, only partly carried out in the stomach, are completed in the small intestine by the **trypsin** of the pancreatic juice, and the peptones (or amino-acids into which they are split) pass through the intestinal wall into the circulation. The **casein** of milk, being in colloidal suspension, is completely hydrolyzed to peptones in the stomach.

When heated, as in *cooking,* the proteins do not behave alike. Some, like albumen (white of egg), become coagulated, though probably *not* less digestible. The same is true of the blood proteins (hæmoglobin, etc.) of beef. On the other hand, the connective tissue of meat (chiefly **collagen**) is insoluble in cold water, but in hot water goes into colloidal suspension as **gelatine.** It is therefore softened by judicious roasting (underdone meat), provided the operation is not carried so far (overdone meat) that the water in the meat is largely evaporated.

Fuel Value. — While food is needed primarily to replace the material which is continually eliminated from the system, the organism also requires energy to maintain the routine motions of the heart, intestines, lungs, and other organs, and the normal muscular tension, as well as the movements of the muscles in walking and working. If the heat derived from routine changes is not sufficient to maintain the temperature (37° C.) of the body, then additional food material is oxidized by the system for this specific purpose. The values of foods are therefore conveniently estimated in terms of the heat they produce when burned — their **fuel values.**

The average fuel values, as measured in the calorimeter, with certain necessary corrections, and expressed, as is usual in this work, in **large calories*** *per gram,* are Carbohydrates 4 Cal., fats 9 Cal., proteins 4 Cal. The fuel values *per pound* (= 453.6 g.) are 453.6 times greater: Carbohydrates 1800 Cal., fats 4080 Cal., proteins 1800 Cal.

Normal Diet. — There is much uncertainty, as yet, in regard to the best choice of foods, in respect to the exact distribution in kind

* One large calorie (1 Cal.) is equal to one thousand small calories (1000 cal.), as hitherto defined (p. 161) and used.

and quantity. We know, however, that life cannot be maintained on one kind (say sugar or gelatine) alone. A mixed diet is necessary. In general, it appears that 100 g. of proteins (giving 4 × 100 Cal.) per day, and a sufficient amount of other foods to bring the total fuel value up to 2200 Cal. per day, is sufficient for a person leading a strictly sedentary life. For work involving physical exercise, larger values, up to about 3800 Cal., are required.

From the data given in the table (p. 630) the fuel value of 100 g. of each kind of food can easily be calculated.

Fuel Values and Prices of Foods. — If the current prices are considered, one can also readily calculate the fuel value obtainable for a given sum of money invested in each kind of food. Thus: lean beefsteak contains 22.1 per cent of protein, or 0.221 pound per pound of meat. The fuel value of this protein is 0.221 × 1800, or 398 Cal. per pound.

	Price* per 1 Pound, Cents	Fuel Values per 1 Pound				Cal. per 10 Cents
		Protein	Fat	Carbohydrate	Total	
Steak	50	398	118	....	516	103
Eggs	50	266	428	....	694	140
Oatmeal	10	290	294	1215	1799	1800
Flour	10	249	61	1309	1619	1620
Almonds	80	378	2240	311	2929	366
Potatoes	5	40	4	331	375	750
Cheese	50	500	1500	74	2074	415
Sugar	10	...	....	1800	1800	1800

* The prices vary greatly with the quality, the season of the year, the demand, the supply, etc.

Vitamins. — A diet may be carefully balanced with respect to carbohydrates, fats and proteins, and yet lead to malnutrition through deficiency in *vitamins*. These are substances present in minute quantities in most fresh or unsterilized foods, particularly in milk and green vegetables (see Fig. 185), without the aid of which certain parts of the animal mechanism either cease to develop or fail to perform their functions entirely. The three best-known types are:

(1) **Fat-soluble vitamin A,** plentiful in milk, butter, the yolks of eggs, cod-liver oil and the leaves of green plants, but not found

in grains, sugars, or refined vegetable fats and oils. This vitamin * is needed to promote the growth of children; its absence leads to rickets and a disease of the eye called xerophthalmia.

(2) **Water-soluble vitamin B,** plentiful in the *outer hull* of grains, beans, green leaves and fruit and yeast, but not in the *kernels* of

	"A"	"B"	"C"		"A"	"B"	"C"
BREAD, WHITE (WATER)	?	+	—	TOMATOES (RAW OR CANNED)	++	+++	+++
" , " (MILK)	+	+	?	BEANS, KIDNEY	*	+++	*
" WHOLE WHEAT ([illegible])	+	++	?	" , NAVY	*	+++	—
" , " " (MILK)	++	++	?	" , STRING (FRESH)	++	++	++
BARLEY (WHOLE)	+	++	—	CABBAGE, FRESH, RAW	+	+++	+?
CORN, YELLOW	+	++	—	" , COOKED	+	++	+?
OATS	+	++	—	CARROTS, FRESH, RAW	++	++	++
MEAT, LEAN	——+	+?	+?	" , COOKED	++	+	+
BEEF FAT	+	—	—	CAULIFLOWER	+	++	+
MUTTON FAT	+	—	—	CELERY	*	+	*
PIG KIDNEY FAT	++	—	—	CUCUMBER	*	+	*
OLEOMARGARINE	+	—	—	DANDELION GREENS	++	++	+
LIVER	++	++	+	EGGPLANT, DRIED	*	++	*
KIDNEY	++	++	+?	LETTUCE	++	++	+++
BRAINS	+	++	+?	ONIONS	*	++	++
SWEETBREADS	+	+	*	PARSNIP	—?	++	*
FISH, LEAN	—	+	*	PEAS	++	++	+?
" , FAT	+	+	*	POTATOES (BOILED 15 MIN.)	*	++	+?
" , ROE	+	++	+?	" (" 1 HOUR)	*	++	+?
MILK, FRESH	+++	++	+V	" (BAKED)	*	++	+
" , CONDENSED	+++	++	+V	SWEET POTATOES	++	+	*
" , DRIED, (WHOLE)	+++	++	+V	RADISH	*	+	*
" , SKIMMED	+	++	+V	RUTABAGA	—?	++	+++?
BUTTERMILK	+	++	+V	SPINACH, FRESH	+++	+++	*
CREAM	+++	++	+V	" , DRIED	+++	++	*
BUTTER	+++	—	—	SQUASH, HUBBARD	++	*	*
CHEESE	++	*	*	TURNIPS	—?	++	*
COTTAGE CHEESE	+	*	*	APPLES	+	+	+
EGGS	++	+	+?	BANANAS	+?	+?	+
ALMONDS	+	+	*	GRAPE JUICE	*	+	+
COCONUT	+	++	*	GRAPEFRUIT	*	++	++
HICKORY NUTS	*	++	*	LEMON JUICE	*	++	+++
PEANUTS	+	++	*	ORANGE JUICE	+	++	+++
PECANS	*	+	*	PRUNES	*	+	—
WALNUTS	*	++	*	RASPBERRIES ([illegible])	*	*	+++

\+ · · · contains the Vitamin
++ · good source of the Vitamin
+++ · · excellent source of the Vitamin
— · · · no appreciable amount of the Vitamin
? doubt as to presence or relative amount
* evidence lacking or insufficient
V variable

A WELL BALANCED DAILY DIET

1. **Milk**—a quart for a child, a pint for an adult—as a beverage or used in cooking. 2. **Vegetables**—Two daily.
3. **Fresh Fruits**—At least once daily.
4. **Meat, or Fish, or Eggs or Cheese or Beans or Lentils.**
5. **Bread and Cereals**—Preferably whole wheat and other entire grain. 6. **Fat**—Butter or other fat in some form every day.
7. **Sweets**—Best when taken in a moderate amount at mealtime.

FIG. 185. Vitamins in Food.

grains, such as polished or milled rice. Deficiency of this vitamin in the diet leads to boils and skin eruptions and in extreme instances to beriberi. Associated with this anti-neuritic vitamin is a

* More correctly *mixture of vitamins.* Several investigators have recently isolated a Vitamin D, to which the anti-rachitic properties appear to be due.

second growth-promoting component, which is also thought to prevent pellagra.

(3) **Water-soluble vitamin C,** plentiful in citrous fruits, tomatoes, cabbage, lettuce, and other fresh fruits and vegetables. The value of this vitamin lies in the prevention and cure of scurvy. It is easily destroyed, except in the case of acid foods, by heating, drying or aging. Since milk is *neutral,* infants fed entirely on *pasteurized milk* are almost sure to develop a mild case of scurvy unless the diet also includes a little orange juice or some other source of water-soluble vitamin C. Owing to the acid nature of tomatoes, even the canned product is rich in this vitamin.

Remarkable progress has been made recently in connection with the question of vitamins in foods. Rickets, the disease of the bones which affects more than fifty per cent of children in our large cities, has been found to be curable by proper exposure of the sufferers to sunlight or ultra-violet radiation. This discovery has been followed up by the still more remarkable announcement (due to independent work by Dr. Hess of New York and Dr. Steenbock of Wisconsin) that it is possible to cure pronounced cases of rickets in animals merely by exposing the *food* supplied to the animals to ultra-violet radiation. Substances such as oils which ordinarily possessed no curative properties became exceedingly efficient in curing rickets after exposure to ultra-violet light.

Another fat-soluble vitamin, E, has also been reported. It occurs in oil extracted from the germ of the wheat seed and in some green plants; in its absence reproduction in animals ceases.

Animal Products. — Many valuable products, apart from foods, are derived from animal life. The use of animal products in *fertilizers* (calcium phosphate from bones, nitrogen compounds from manure, etc.) has already been discussed (Chapter XXXV).

When bones or dried blood are subjected to destructive distillation (compare p. 622), the residue consists of **animal charcoal.** The charcoal from bones (**bone black**) contains 90 per cent of mineral matter, largely calcium phosphate, and only 10 per cent of carbon. Animal charcoal, being a very active adsorbent (p. 623), is used in *sugar refining* as a decolorizer. When its powers in this direction have been exhausted, it is **calcined** — that is to say, all the combustible matter is burned out of it — and the product is **bone-ash,** which contains about 83 per cent of calcium phosphate. Formerly this was used in making phosphorus, but now the less expensive calcium phosphate of fossil origin (p. 541) is employed.

The basis of **wool,** and of hair fibers in general, is a protein called *keratin.* The **silk** fiber is also of animal origin, but differs very widely from wool in its structure and properties. As spun by the

silkworm in the preparation of its cocoon, it consists of two filaments composed of a protein called *fibroin* surrounded and cemented together by a gluey substance known as *sericin* or silk-gum.

Glue, an impure form of gelatine (p. 635), is obtained from the skin and bones of animals by extraction with water under pressure. **Leather** is prepared from the hides by tanning (see p. 878).

Casein, a protein contained in milk and precipitated therefrom by dilute acids, has recently found many interesting applications. In the modified form of cheese, of course, it has long been of value as a food. Mixed with various alkalies it gives *glues, cements* and *plastics*. It is used as an ingredient in *paints*, and for *sizing* or *enameling* paper. Paper bottles are made waterproof by impregnating them with casein and then exposing them to the vapor of formaldehyde (p. 582). *Galalith* (milk-stone) is a plastic harder than celluloid (p. 652) and non-inflammable, made by the same hardening action of formaldehyde on casein.

Soap. — When fats are hydrolyzed by heating with a solution of *caustic soda* NaOH, instead of water, *the sodium salts of the acids are obtained.* These sodium salts are known as **soaps** and the operation is called **saponification:**

$$\underset{\text{palmitin}}{C_3H_5(CO_2C_{15}H_{31})_3} + 3NaOH \rightarrow \underset{\text{glycerine}}{C_3H_5(OH)_3} + \underset{\text{sodium palmitate}}{3Na(CO_2C_{15}H_{31})}.$$

The sodium palmitate or other soap is *apparently* (see p. 642) soluble in the water. When common salt is added, however, the soap coagulates and separates into a floating layer which solidifies on cooling.

Soft soap is made with potassium hydroxide, and is composed of the potassium salts of the organic acids.

Manufacture of Soap. — Soap is made in large iron cauldrons. These contain closed steam coils for heating, and pipes delivering live steam, when needed, for stirring the mass. The fat is mixed with caustic soda solution containing, at first, only about one-fourth of the total amount of the base that the above equation requires. When, after heating and stirring, a uniform mixture has been produced, the rest of the alkali is added gradually and the heating is continued until the reaction appears to be complete. Salt is now dissolved in the mixture and the soap separates as a curd. The curd floats, leaving the "spent lye," containing the salt solution and much of the glycerine, in the lower layer. This process is called **salting out.**

When the process stops at this point, the upper layer is known as **curd soap,** and may be dipped out and allowed to cool and solidify. Most "Marseilles" soaps are curd soaps made in this way. A large part of the imported "Castile" soaps are of the same kind.

Curd soaps contain salt, glycerine, adhering lye, and other impurities. To prepare a purer soap, the spent lye is run off, dilute brine is added to the soap, and the curd and brine are stirred up. When separation has again occurred, the brine is run off and the process repeated. Finally, some water is added, and steam is run in until the curd mixes completely with the water. When the solution stands, it "settles," that is, resolves itself once more into two distinct layers. The upper layer is called **settled soap.** The washing with brine and temporary dissolving in water remove the impurities, and hence settled soap is the purest variety. The greater part of the soap made in the United States and in Great Britain is of this kind.

The qualities of soaps are varied by adding "fillers," such as sodium carbonate, borax, or sodium silicate. **Soap powders** are often made of ground soap mixed with sodium carbonate. Dyes and perfumes are sometimes added to soaps. Air bubbles are mixed with the soap, by beating, to give the floating varieties. Soap for scouring contains fine sand. Transparent soaps are made by dissolving the soap in alcohol, or by the addition of glycerine or sugar.

Chemical Properties of Soaps. — The soaps, being sodium salts of weak acids, exhibit the *usual reactions of such salts* in aqueous solution. Thus, when a strong acid is added, double decomposition takes place:

$$\underset{\text{sodium palmitate}}{Na(CO_2C_{15}H_{31})} + HCl \rightarrow NaCl + \underset{\text{palmitic acid}}{H(CO_2C_{15}H_{31})} \downarrow.$$

The *acids,* being insoluble, are thrown down as white precipitates.

When other salts are added, similar actions may occur. Thus with calcium chloride solution, calcium palmitate is precipitated:

$$2Na(CO_2C_{15}H_{31}) + CaCl_2 \rightarrow 2NaCl + Ca(CO_2C_{15}H_{31})_2 \downarrow.$$

This action is important in connection with "hardness" in water (p. 730). The fact that even sodium chloride, which cannot react in this way, precipitates soaps (p. 639) indicates, however, that we have not here a case of simple solution. To explain the properties of soaps completely, a brief digression into the subject of colloids will be necessary.

Colloidal Suspension. — We have seen (p. 602) that starch can be suspended in water in such a fine state of division that the liquid is transparent, and *runs through a filter* without leaving any solid on the paper. Yet this "colloidal suspension" lacks some of the characteristic properties of a solution.

The simplest proof that this is a case of imitation solution, and not of true solution (molecular dispersion, p. 198), is obtained by examining the liquid with the **ultra-microscope.** A converging beam of strong light is sent through the liquid *horizontally* (Fig. 186), and the illuminated place is viewed *from above* through a microscope. When the room is dark, and the only light comes from the horizontal beam, a colloidal suspension shows minute points of light. A true solution — such as one of common salt or of alcohol — remains perfectly dark. The points of light (compare p. 459) are produced by myriads of *suspended particles,* which, although extremely minute, are of far larger than molecular dimensions. Solutions of soap, gelatine, and many dyes, blood serum, and innumerable other liquids contain such suspended particles.

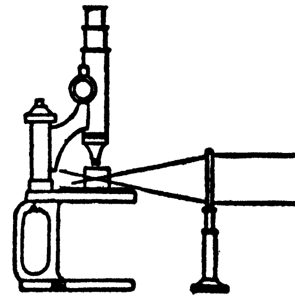


FIG. 186. Ultra-microscope.

The particles of a colloid (like starch), when viewed in this way, show a continued unordered, zigzag movement (**Brownian movement**), which is more rapid the smaller the particles, and is due to the impacts of the molecules of the solvent.

The simplest colloidal suspensions are those of metals like gold and platinum. They can be made by forming an electric arc between the points of two wires, while the points are immersed in water to which a very small trace of sodium hydroxide has been added. Liquids of various colors, depending on the degree of **dispersion** (fineness of the particles) of the metal, are thus formed.

Other Properties of Colloidal Suspensions. — The freezing-point, boiling-point and vapor tension of a liquid containing a colloid in suspension are all practically *identical* with those of the pure solvent. This is quite different from what we have seen to be the case with true solutions (pp. 211–7), and indicates that the fraction of the "solute" particles present is substantially *zero.* The unit particles of suspended material, indeed, are complex aggregates so much larger than the ultimate molecules into which true solutes are broken up that the number of them present in the solution, compared with the number of solvent molecules, is entirely negligible.

When a "solution" of a colloid is placed in a "diffusion-shell" of parchment, surrounded by pure water, *none of the colloid escapes* through the minute pores of the shell. Ordinary, non-colloidal solutes do escape, more or less rapidly (salt rapidly, sugar slowly, see p. 608). In this way a *mixture of colloid and non-colloid* (say, starch and salt) *can be separated,* if the water surrounding the shell is replaced by pure water at intervals until all the non-colloid has been removed. This method of separation is called **dialysis.**

When wires from a battery are immersed in the liquid, the particles of a colloid are found to move slowly towards either the cathode or the anode. The phenomenon is called **electrophoresis.** Apparently, the colloidal particles are aggregates of molecules of an insoluble substance, associated with one or more ions. The particles, although relatively large, move almost as rapidly as in ionic migration (p. 311). This affords an explanation of the fact that the particles remain suspended, and do not settle. They are individually so small that they are kept in motion by collisions with the molecules of the solvent. If they could unite into still larger aggregates — like the particles of a precipitate — they would separate like any ordinary, insoluble substance. But, having like electrical charges, they *repel* one another, and so remain separate and in suspension.

Now most colloids can be readily **coagulated** or flocculated, and so precipitated in the liquid, by adding a solution of an ionized substance. Thus, colloidal gold and other metals are negative, and a (small) equivalent amount of a positive ion, usually H^+, is present also. When a salt is added, the ionic concentration in the solution is greatly increased, the positive ion of the salt attaches itself to the negative colloidal metallic particles, neutral bodies result, coagulation can now occur, and precipitation follows. Bivalent ions are more effective than univalent ones. Conversely, a positive colloid, like ferric hydroxide, is coagulated by the negative ion of a salt, and more easily the higher the valence of the negative ion.

Starch and gelatine are coagulated with much greater difficulty. They are known as **lyophilic** (=solvent-loving) as distinguished from the **lyophobic** (=solvent-hating) colloids mentioned above, and presumably form unstable complexes with water which assist to keep them in suspension.

Even a lyophilic colloid, such as albumen, can be coagulated, however, by another colloid of opposite charge. Thus, metaphosphoric acid is a negative colloid when in solution, while ortho- and pyro-phosphoric acid are not colloidal. Albumen, as ordinarily prepared, is a positive colloid. Hence (p. 554), metaphosphoric acid and albumen coagulate and precipitate one another, while the other two acids have no action on albumen.

Colloidal Matter in Soap Solutions. — The distinction between "colloidal suspensions" and "true solutions," like the distinction between polar and non-polar compounds (p. 149), is one of degree only, and soaps are substances which fall between the two classes in their behavior. The freezing-point of a soap solution is depressed below that of water, but not nearly so much as we should expect for a fully-ionized salt (p. 295). The capacity for being coagulated and precipitated by electrolytes, which is characteristic of colloidal matter, is shown very clearly by soap solutions. This

explains the process of "salting out" (p. 639) which plays so large a part in the manufacture of soap.

If we examine the formula for a typical soap, *e.g.*, sodium palmitate $C_{15}H_{31}.COONa$, we see that it consists of two parts: a long non-polar hydrocarbon chain ($C_{15}H_{31}$—) and a polar tail-piece (—COONa). It is to the antagonistic tendencies of these two portions of the molecule that the special properties of soap solutions are due. The polar end tends to go into true solution, and to form the ions —COO^- and Na^+. The non-polar hydrocarbon chain, however, has no greater tendency to dissolve in water than a fat or oil itself. It tends, rather, to remove itself from an aqueous environment entirely. The two tendencies compromise in the formation of electrically-charged aggregates which have been called "ionic micelles."

At the surface of a soap solution, the soluble polar tail-piece (—COONa) will be attracted *inwards* by the water molecules, while the insoluble hydrocarbon chain ($C_{15}H_{31}$—) will be repelled *outwards*. The surface of a soap solution with a greater concentration than 0.002 *N*, indeed, is essentially a continuous hydrocarbon surface; so marked is this effect. The surface tension of the solution is consequently the low surface tension of a typical oil, instead of the high surface tension of water.

The chief use of soap solution is in removing grease and dirt from yarn, cloth, or clothing, and from woodwork and kitchen utensils. Soap solution has *two* more or less distinct properties, *one* of which enables it to remove oil or grease (viscous, insoluble liquids), and the *other* of which enables it to remove dust and dirt (largely minute, solid particles of carbon or soot). The former is its *emulsifying power*, the latter is connected with its nature as a *colloidal suspension.*

The Emulsifying Action of Soap. How Soap Removes Grease.—When an insoluble oil, such as kerosene or lubricating oil, is shaken with water, it is divided into minute droplets separated by water from one another. Immediately the shaking ceases, the droplets begin to run together and soon the oil and water have separated once more into two layers of transparent liquid. When very dilute soap solution and oil are shaken together, however, the droplets do not run together, but remain permanently suspended. The surface of the soap solution in contact with each oil droplet is itself, as explained above, essentially an "oil," and the rigid film at the interface renders any separation exceedingly difficult. The

mixture is opaque and more or less viscous. Such a **permanent mixture of two insoluble liquids** is called an **emulsion** (compare p. 198).

Soap solution, when *rubbed* on oily or greasy goods, *emusifies the grease,* converts it into droplets, surrounded by soap solution and separated from the cloth, and so permits it to be washed off.

In mayonnaise dressing, which is a thick, almost solid, permanent emulsion, the olive oil is emulsified by the colloidal matter of the yolks of the eggs which have been beaten into the vinegar.

How Soap Removes Dirt. — When a solution containing colloidal substances, such as many dyestuffs and organic coloring matters, is shaken with finely pulverized charcoal, the colloidal aggregregates adhere to the surface of the powder (are **adsorbed**) and the liquid is consequently decolorized (see p. 623).

When dilute soap solution is shaken with diatomaceous earth (p. 660) and the mixture is filtered, the clear liquid is found to have been deprived of the soap. The soap is evidently precipitated (adsorbed) on the surface of the particles of the solid.

Clearly there is a tendency to cohesion between the colloid in a soap solution and the particles of a fine powder. When there is much of the powder, and little of the soap in solution, the powder takes the soap out of the solution. When, however, there is much of the colloid in the form of soap solution, and little of the solid, and that very finely divided, the same tendency to adsorption exsists, *only, in this case, the colloidal particles carry off the powder.* In short, the dirt is removed into the solution.

Formerly soap solution was supposed to remove grease (and soot?) because of its slight alkaline reaction, due to hydrolysis. This explanation must be given up because: (1) an alkali so dilute that it exists in equilibrium with the free fatty acid, cannot possibly saponify the *ester* contained in a grease spot. (2) Pure alkali of the same concentration (or stronger) has no more emulsifying power than water. Such an alkaline solution will indeed emulsify an animal or vegetable oil (cod-liver oil, cotton oil, castor oil), but it does so by interacting with the free fatty acid always present in such oil (p. 633) and *forming therefrom a soap.* Such an alkaline solution does *not* emulsify kerosene, although soap solution does. The emulsifying agency is always a soap. (3) Very dilute alkali has no more effect upon soot than has water — but soap solution takes clean (greaseless) soot instantly into permanent suspension.

The power of forming an emulsion depends, theoretically, upon the *abnormally low surface tension* of dilute soap solution. Very dilute alkali has the same high surface tension as has pure water.

Exercises. — 1. Make equations for the formation: (*a*) of maltose from starch; (*b*) of glucose from maltose.

2. Make a connected statement showing the stages in the digestion of milk.

3. Why does fat appropriately form a larger proportion of the diet in the Arctic regions than elsewhere?

4. Give the weights of carbohydrate, protein, and fat which would supply a menu, such that the total food value was 3000 cal., that 100 g. of protein was included, and that the remaining fuel value was divided equally between carbohydrates and fats.

5. Calculate the calorific value of 1 kg. of: (*a*) wheat flour; (*b*) oatmeal.

6. (*a*) In what proportions by weight should baking soda and cream of tartar be used in raising bread? (*b*) What is the objection to using too large a proportion of baking soda? (*c*) Why must baking powder be kept in a dry, cool place?

7. Why does vinegar liberate carbon dioxide from baking soda? Make the equation for the action.

8. Make equations for the formation of: (*a*) ethyl formate; (*b*) glyceryl formate; (*c*) ethyl stearate.

9. Make equations for the action of superheated water on: (*a*) stearin, and (*b*) olein; and for the action of caustic soda on: (*c*) stearin, and (*d*) ethyl acetate.

10. Summarize the facts which show soaps to be salts.

11. (*a*) Write the full equation for the hydrolysis of sodium palmitate. (*b*) What reaction (acid or alkaline) should soap solution possess, and why (p. 640)?

12. Why does "French dressing" (vinegar, salt, and olive oil) give an emulsion, which is much less durable than mayonnaise dressing?

13. Given a dilute solution of sodium hydroxide, how could you make an immediate distinction between an artificial fat, such as hydrogenated cottonseed oil (p. 634), and solid paraffin (p. 579)? Discuss your method in detail.

14. Write the structural formula for glycerine. (The hydroxyl groups are all attached to different carbon atoms.) In what respects does glycerine remind us of a base? Why do we not consider the substance to be a true base?

15. Tabulate the examples of catalytic reactions that you have encountered in Chapters XXXIV–XXXVII, noting the nature of the catalyst in each case.

16. What differences exist between vegetable oils (p. 632) and mineral oils (p. 578), (*a*) in constitution, (*b*) in chemical properties? Why are mineral oils useless for food purposes?

17. Devise two methods of proving that particles of arsenious sulphide, in colloidal suspension, are electrically charged, and that their charge is negative.

18. To a beaker full of boiling water, a few c.c. of concentrated ferric chloride solution are added. Formulate the reaction that occurs (p. 905). How could you prove that you had a colloidal suspension of ferric hydroxide?

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CHAPTER XXXVIII

SYNTHETIC ORGANIC PRODUCTS

A brief summary of the more important of the many thousands of organic products manufactured in the laboratory is all that can be presented here. The products included are, on the *constructive* side, **dyes, perfumes, drugs** and **plastics** (including **rubber**); on the *destructive* side, **explosives** and **toxic gases.**

Some dyes, perfumes and drugs are still, of course, obtained from natural sources, and synthetic rubber continues to show but little promise of superseding plantation rubber in the near future. Nevertheless, the interest of the chemist in the fields here under discussion is almost entirely *synthetic,* seeking to duplicate natural products by laboratory methods and to discover new products of even greater use to humanity.

Dyeing. — The problem of the dyer is to confer the desired color upon a fabric made, usually, of cotton, linen, wool, or silk, and to do this in such a way that the dye is *fast* to (*i.e.*, is not removed or destroyed by) rubbing and light, and often, also, to washing with soap. To understand the means by which this is achieved, it must be noted that cotton and linen consist of smooth hollow fibers (A, Fig. 187) of cellulose. Wool (B) is made of hollow fibers with a scaly surface, and silk of solid filaments, but both these substances are composed of proteins (pp. 597, 638). Now, the proteins are much more active chemically than is cellulose, and also, as colloidal materials, seem to have a much greater tendency to adsorb other substances (compare p. 644) than has cellulose. Hence, accidental stains on wool or silk are much less often removable than are those on cotton, and when samples of the three materials are dipped in a solution of a dye, the first two are permanently dyed, while from the last most dyes can be completely washed out with water.

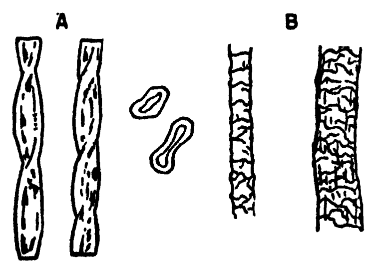


FIG. 187. Cotton and Wool Fibers.

Three modes of dyeing may be mentioned:

1. **Insoluble Dyes.** If the colored body can be produced by precipitation, after the solution has filled the capillary and wall of every fiber of the goods, then, if the dye is sufficiently insoluble, it is mechanically imprisoned in every fiber and cannot be washed out. This plan may be applied to any kind of goods. For example, if cotton, silk, or wool is first boiled in a solution of lead acetate, and is then soaked in a boiling solution of potassium chromate K_2CrO_4, it is dyed a brilliant, permanent yellow. Lead chromate (**chrome yellow**) is the colored body:

$$Pb(CO_2CH_3)_2 + K_2CrO_4 \leftrightarrows 2K(CO_2CH_3) + PbCrO_4 \downarrow.$$

The part precipitated on the outside of the goods can be, and is, at once washed off by rubbing in water, but the particles inside the fibers can come out only by being dissolved, and they are insoluble in water. **Indigo** $C_{16}H_{10}N_2O_2$, which is used in larger amounts than any other dye, belongs to this class. Obtained in early times from several points in Europe and Egypt, where it was known as woad, and more recently imported from India, where the cultivation of the indigo plant was as important an industry as is the growing of cotton in the Southern States, it is now almost all made artificially. The cloth is saturated with an alkaline solution of indigo white $C_{16}H_{12}N_2O_2$, a soluble, slightly acid substance, and the oxygen of the air subsequently oxidizes this and deposits the insoluble indigo blue within the fibers:

$$2C_{16}H_{12}N_2O_2 + O_2 \rightarrow 2C_{16}H_{10}N_2O_2 \downarrow + 2H_2O.$$

2. **Mordant or Adjective Dyes.** Since cotton is inactive chemically and has but a slight tendency to adsorb dyes, it is usually necessary first to introduce into the fibers of cotton some colloidal substance with greater adsorptive powers. Substances of this kind are *tannic acid* (p. 909) for basic dyes, and *gelatinous colloidal hydroxides,* such as those of aluminium, tin, iron and chromium, for non-basic (including acid) dyes. They are called **mordants** (Latin, *mordere,* to bite). Thus, if in three jars we place very dilute solutions of aluminium sulphate, ferric chloride $FeCl_3$ and chromous acetate $Cr(CO_2CH_3)_2$, then add a few drops of a solution of a dye to each, and finally introduce a little of a base (like sodium hydroxide) to precipitate the hydroxide of the metal, this hydroxide will adsorb the dye and carry it into the precipitate.



Courtesy of Dow Chemical Company

MANUFACTURE OF SYNTHETIC INDIGO

See page xxiii



THE FIRST HUMAN PORTRAIT

Artotype copy of the earliest sunlight picture of a human face.

Miss Dorothy Catherine Draper, taken by her brother, Professor John William Draper, M.D., LL.D., of the University of the City of New York early in 1840. The original daguerreotype is the property of Sir William John Herschel of England.

See page xxiv

Such a precipitate of mordant and dye is called a **lake.** With the same dye, the three lakes have different colors. Thus, in the above-mentioned experiment, if **alizarin** $C_{14}H_8O_4$ (madder) is used as the dye, the colors are red (Turkey red), violet, and maroon, respectively. This is probably due to the different degrees of dispersion in the three colloidal materials. Basic dyes, like **Malachite green** and **Methylene blue,** behave similarly with tannic acid, or an insoluble salt of tannic acid, as mordant. It will be seen that, so far as the fabric is concerned, this process, like the first, is a mechanical one, and is independent of the chemical nature of the goods.

3. **Direct or Substantive Dyes.** Most organic dyes are direct dyes on silk or wool, and require no mordant with these materials. The actions seems to be sometimes chemical, but more often cases of adsorption by the silk or wool (both colloids) themselves. A few dyes are also fast on cotton. **Congo-red** is fast both on cotton and wool, but is no longer much used. **Chrysophenin** is now one of the commonest dyes of this class. These dyes, which are sodium salts of complex organic acids, are *colloids* like soap (p. 642), and are salted out within the fibers of the goods by adding sodium sulphate to coagulate them and assist the adsorption by the cotton. Once adsorbed in this way, unlike soap, they cannot be washed out.

Dye-Stuffs. — Natural dye-stuffs have now been almost entirely superseded by manufactured products, which can be prepared more cheaply and are of superior quality. **Logwood,** still used as a black mordant dye for silk, is the only important exception.

The vast bulk of synthetic dyes are built up from ring hydrocarbons (p. 587) and their derivatives, extracted from coal tar (p. 625). By substituting suitable groups into the molecule of the simpler *colorless* products, more complex derivatives with great brilliancy of color may be obtained. Thus **indigo,** formerly the most extensively used of all natural dyes, is now manufactured most conveniently with aniline $C_6H_5.NH_2$ as a starting point. **Alizarin** (Turkey red), once extracted from *madder root,* is obtained from anthracene.

By varying the position of the substituted groups in the molecule, the most delicate variations in color can be effected. The most precious of all dyes in ancient times was *Tyrian purple,* obtained from certain species of sea snails (*Murex*). The secret of preparing this substance was lost for centuries, but in 1909 Friedlaender gathered 12,000 of these mollusks and succeeded in isolating 1.5 grams of the coloring material for analysis. He showed it to

be a *derivative of indigo,* containing two bromine atoms in place of two of the hydrogens. This identical substance had been prepared synthetically five years earlier, but found to be *inferior* to another dye containing the bromine atoms in different positions in the molecule!

Perfumes. — Many natural perfumes and fruit flavors can also be produced synthetically. The basis of most of these consists of **esters** (p. 583). The fragrance of ripe *apples* is due to minute amounts of the amyl esters of formic, acetic and caproic acids. In *bananas* the characteristic ester is amyl acetate; in *grapes* it is methyl anthranilate. *Almond* flavor is due to benzaldehyde, $C_6H_5.CHO$; the smell of *geraniums* to diphenyl ether, $(C_6H_5)_2O$. The chief ingredient of *otto of roses* is geraniol; of the *vanilla* bean, vanillin; of the perfume sold as *"new mown hay,"* coumarin; all complex hydrocarbon derivatives which are now commercial products. Some of the synthetic flavors and perfumes on the market are identical with the substances that give odor to fruits and flowers; others are merely more or less adequate imitations. Thus, natural *oil of wintergreen* is essentially the same as synthetic methyl salicylate. On the other hand, amyl valerate, which is sold as *apple essence,* is not contained in the fruit, though it smells like it. Most perfumery nowadays, including the most expensive, consists of mixtures of natural and synthetic products.

Drugs. — In the same way, many drugs formerly obtained from natural sources are now built up in the laboratory, and many new compounds have been made which possess as valuable medicinal properties as any found in nature. The first stage in this work consisted in determining the constitution of the active ingredients of plant products. *Quinine* was isolated from cinchona bark, *morphine* from the seed capsules of the opium poppy, *strychnine* from the seeds of *nux vomica.* These and other substances of similar character are now classed together as **alkaloids,** complex nitrogenous substances possessing basic properties. The structure of many of the alkaloids is now completely worked out. It is not necessary, however, to synthesize the entire complicated molecule if the same results can be secured with simpler substances, and this has been demonstrated already in many instances.

Aspirin is an ester of salicylic acid $C_6H_4.OH.COOH$; *acetanilide* is a derivative of aniline $C_6H_5.NH_2$. *Novocaine,* prepared from diethylaniline, has practically replaced the natural alkaloid

cocaine in dentistry. *Saccharin* is obtained from toluene; its solution in water has an intensely sweet taste, hence it is used as a substitute for sugar in cases of diabetes. It has no food value, however, and hence cannot replace sugar in nutrition.

Plastics. — These are substances, like celluloid, which can be molded or shaped into any desired form. Among natural plastics may be mentioned resins, gums, and rubber.

The rubber **latex,** collected from the tree, is first freed from its water by heat. The residual material is sticky and soft when hot, hard and brittle when cold. To bring it into a state where it can be conveniently used, **vulcanization** is necessary. This process, invented by Goodyear in 1839, consists in heating the rubber with a small percentage of sulphur to 140° until the desired properties have been acquired. During the process a chemical reaction takes place between the sulphur and the rubber which is not yet completely understood. The time necessary for vulcanization may be materially shortened by incorporating with the mixture an **accelerator** — usually an organic base of suitable strength, which functions as a catalyst. Other ingredients (*e.g.*, white lead, zinc oxide, antimony sulphide, or lampblack) are added to the rubber at various stages in its manufacture, as fillers or pigments, according to the exact qualities required in the finished product. Synthetic rubber equal to the natural product in durability and cheapness has still to be prepared (see p. 712), but many other synthetic plastics are now of considerable industrial importance.

Certain *cellulose* plastics have already been described (p. 601). Cellulose behaves chemically like an *alcohol,* and as such forms *esters* with acids (see p. 583). When cotton is treated with acetic acid (in the form of acetic anhydride $(CH_3.CO)_2O$, see p. 383), it gives **cellulose acetate.** The viscous liquid dries to a tenacious film. On account of its weatherproof character, non-inflammability and non-conductance of electricity, it is now extensively used for coating the wings of aeroplanes ("dope"), for making moving-picture films, and for insulating electric wires. It constitutes a very important form of rayon or artificial silk (**celanese**). Artificial horsehair and bristles for hair brushes are also made of it.

By the action of nitric acid upon cellulose, various *cellulose nitrates* may be formed, according to the number of OH groups replaced by NO_3 (see guncotton, p. 653). Plastics containing these nitrates are known generally as **pyroxylins.** An incompletely ni-

trated ester, when worked between rolls with camphor * and a little alcohol, forms a viscous solution. When the alcohol evaporates, a transparent colorless solid, **celluloid,** remains. Photographic films are made by rolling the dough into sheets. Fillers and dyes can be added to the dough and the latter can be molded to any form. In this way ivory-like or black combs and brush handles, opaque white knife handles, articles of "artificial amber" and so forth can be made.

The same sort of guncotton dissolves in a mixture of alcohol and ether, giving a solution called **collodion,** used in photography and in medicine. In **automobile lacquers** a suitable mixture of high- and low-boiling organic solvents, together with other substances which function as plasticizers, stabilizers, and pigments, is employed as a medium for obtaining a thin coating of cellulose nitrate on the metal or wood. Artificial leather (**fabrikoid**), used extensively for cushions, for automobile tops, and for book covers, is also a pyroxylin product.

Another plastic, not chemically related to the preceding, is **bakelite,** prepared from formaldehyde CH_2O and phenol C_6H_5OH (carbolic acid). Under suitable heat treatment the mixture gradually sets to a solid, hard, infusible, resinous mass, which is insoluble in all common solvents. Before it sets, it can be dyed or "filled," and it can be applied as lacquer, or molded to any form. Switchboards, dolls, ornamental buttons, artificial jewels, phonograph records, radio accessories, billiard balls, and stereotyping matrices are amongst the objects into which it is now fashioned.

Explosives. Nitroglycerine. — Some inorganic explosives, *e.g.*, ammonium nitrate (p. 538), have been discussed in earlier chapters. The main organic explosives are also compounds of nitrogen.

As already mentioned the alcohols interact with inorganic acids, as well as with organic ones, to produce esters. A familiar illustration is met with in the manufacture of **nitroglycerine** (glyceryl trinitrate) by the action of glycerine and nitric acid:

$$C_3H_5(OH)_3 + 3HNO_3 \rightarrow C_3H_5(NO_3)_3 + 3H_2O.$$

To assist in the liberation of the water, the nitric acid is mixed with a dehydrating agent (sulphuric acid). The glycerine is then

* A white solid with the formula $C_{10}H_{16}O$, obtained commercially by distilling with steam the wood of the camphor tree, but recently also prepared synthetically.

added slowly to the cooled reagents. The nitroglycerine is an almost *colorless oil* which floats to the surface of the acid mixture. It is shaken repeatedly with water, in which it is insoluble, and then with sodium carbonate solution, in order to free it from all traces of the acids.

Nitroglycerine *explodes* violently, often from the slightest shock. It owes this power to the fact that its carbon and hydrogen can combine with the oxygen it contains to form carbon dioxide and water:

$$4C_3H_5(NO_3)_3 \rightarrow 12CO_2 + 10H_2O + 6N_2 + O_2.$$

The latter are very stable substances and much heat is liberated in forming them. They are both produced as gases and, at the high temperature of the action, they and the nitrogen tend to occupy a great volume — or to exert an enormous pressure in the effort to do so.

The explosion is also so *sudden*, compared with that of gunpowder, that nitroglycerine would shatter the breech of a rifle before the bullet had time to move. It also pulverizes rock, instead of breaking it into fragments of usable size. For these reasons, as well as on account of the danger in handling, and impossibility of safely transporting the substance, it is usually made into dynamite (see p. 654).

That nitroglycerine is a more sensitive explosive than gunpowder is due to the fact that, in the former, the materials required for the chemical change are already within the same molecule, whereas in the latter (p. 702) they are contained in the separate molecules of a mixture. Even after the most careful incorporation, the oxygen of the potassium nitrate can never be uniformly so near to the carbon, mechanically mixed with the salt, as are these elements in nitroglycerine or guncotton. In the latter the oxidation of the hydrogen and carbon is intramolecular.

Substances like hydrazoic acid (p. 515) and nitrogen iodide (p. 518) might seem to constitute a third kind of explosive. Here the change consists in the resolution of the compound into its constituents. Still, if we consider the case of hydrazoic acid, for example: $2N_3H \rightarrow 3N_2 + H_2$, we see that the action consists, after all, in the union of the constituents to form the more stable combinations N_2 and H_2. It is, therefore, similar in principle to the explosion of nitroglycerine.

Guncotton. — When cotton is steeped for half an hour in a cooled mixture of nitric and sulphuric acids, it is converted into cellulose trinitrate or **guncotton:**

$$C_6H_7O_2(OH)_3 + 3HNO_3 \rightarrow C_6H_7O_2(NO_3)_3 + 3H_2O.$$

The equation, as written above, shows that three hydroxyl groups

OH in the empirical cellulose formula $C_6H_{10}O_5$ are replaced by three nitrate groups NO_3, with simultaneous formation of three molecules of water. The sulphuric acid hastens the reaction and carries it to completion by acting as a dehydrating agent (see p. 427). The fibers have the same appearance as before, but are crisper to the touch. The guncotton is washed thoroughly with water to remove the acids, which would cause slow decomposition and perhaps accidental explosion.

Dried guncotton burns briskly (deflagrates) when set on fire. While wet, it can be molded and cut without danger. It explodes only when "set off" by a small amount of another explosive. Fulminate of mercury $Hg(ONC)_2$, used in percussion caps, is commonly employed. By such means the explosion is brought about in wet guncotton as easily as in dry.

In pure form guncotton is used only in torpedoes and submarine mines. It explodes too rapidly to be used in fire-arms or for blasting.

Smokeless Powder and Dynamite. — The violence of guncotton is reduced by compressing it, and still more by dissolving it and allowing the solvent to evaporate. Thus, **cordite** is made by dissolving guncotton (65 parts), nitroglycerine (30 parts) and vaseline (5 parts) in acetone (p. 583). The resulting paste is rolled and cut into pieces of different dimensions, according to the rate of explosion desired. When the acetone evaporates, the horny cordite remains. These explosives are smokeless because they differ from gunpowder (p. 702) in yielding no solids when they decompose.

Blasting gelatine, giant powder, and other forms of **dynamite** are made by dissolving guncotton in nitroglycerine. Substances like ammonium nitrate and sawdust are added to adjust the rate of explosion so that, for example, coal may be split up, but not shattered.

High Explosives. —These are substances which develop their explosive effect at an extremely rapid rate, and are used therefore when a shattering effect of great violence is required, for example in *shells* or in *anti-submarine depth charges.* **Trinitrotoluene** (TNT) is made by nitrating *toluene* (p. 587), **picric acid** (trinitrophenol) by nitrating *phenol* (p. 587). Picric acid * is a strong

* Picric acid is an interesting example of the close interrelation of synthetic organic compounds. It is used in dyeing to give a yellow color, in warfare as an explosive and in medicine as an antiseptic. It may happen that picric acid is used in a base hospital to cure the wound that picric acid caused.

acid and forms salts which, with the exception of ammonium picrate, are more sensitive to shock and friction than the acid itself. The action of this explosive on the metals with which it comes in contact must therefore be guarded against. TNT, however, is inert towards metals, and is insensitive towards ordinary shocks. It melts at a low temperature (80°), and so can be readily liquefied and poured into shells. Mixed with ammonium nitrate, it gives **amatol** (p. 509).

Potassium perchlorate $KClO_4$ (p. 387) was employed to a minor extent during the World War as an explosive. It has an extremely rapid explosion wave, which makes it suitable for use in depth bombs against submarines and in mines against trench systems, but is too susceptible to shock for use in shells.

Toxic Gases. — The poisonous substances employed in the Great War were mainly synthetic organic products. Most of these, it is true, were not gases, but liquids or solids of low volatility. Their vaporization was, however, favored by the explosion of the shell in which they were contained, part of the material being converted to gas by the heat of the explosion and the remainder being scattered around in a finely divided condition. Some of the compounds used were so powerful in their action upon the human system that a concentration of 1 part in 10,000,000 in the air was sufficient to incapacitate anyone unprotected with a gas-mask.

The first method made use of in gas warfare was to release a highly volatile poisonous substance (*chlorine* or a mixture of chlorine and *phosgene* $COCl_2$) from cylinders under pressure. A cloud of gas was thus evolved, which under favorable wind conditions was carried over the enemy's lines. This *cloud* method was soon abandoned in favor of the *shell method* described above. Among the substances thus employed may be mentioned *chlorpicrin* $CCl_3.NO_2$ (made by the action of bleaching powder and lime upon picric acid), and *mustard gas* $(CH_2Cl.CH_2)_2S$. The latter substance, the chemical name of which is dichlordiethyl sulphide, may be regarded as diethylether (p. 584), in which oxygen is replaced by sulphur and two hydrogen atoms are replaced by chlorine. It was produced by the action of ethylene C_2H_4 upon sulphur monochloride S_2Cl_2.

Both of the above substances are actually toxic, that is, a sufficient concentration will induce death. Many other substances were used, however, which merely put the victim temporarily out of action. Among these were *lachrymatories* (tear-producing substances) such as benzyl bromide $C_6H_5.CH_2Br$, and *sternutatories*

(sneeze-producing substances) such as diphenylchlorarsine $(C_6H_5)_2$-AsCl. The latter substance is a derivative of arsine AsH_3 (p. 859), the three hydrogen atoms being replaced by two phenyl groups C_6H_5 and one chlorine. Mustard gas in very low concentration also acted as a skin irritant.

The methods employed for obtaining protection against toxic gases have already been discussed (p. 623).

Exercises. — 1. Write graphic formulæ (see Chapter XXXIII) for the following synthetic essences: ethyl formate, ethyl butyrate, benzaldehyde, diphenyl ether.

2. What chemical change would occur after mixing nitroglycerine with sodium hydroxide solution? Name the kind of reaction and give the equation.

3. When nitroglycerine explodes, in what relative volumes are steam, carbon dioxide, and nitrogen produced? What principle is used in answering this question?

4. Make an equation for the decomposition of guncotton similar to that given for nitroglycerine (p. 653).

5. Make an equation for the denitration of guncotton by an alkali.

6. Write the graphic formulæ for the following substances: acetic anhydride, trinitrotoluene, picric acid, phosgene, chlorpicrin, mustard gas, benzyl bromide, diphenylchlorarsine.

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CHAPTER XXXIX

SILICON AND BORON

In respect to **chemical relations** there is a close resemblance between silicon and carbon. Silicon gives a monoxide, but is quadrivalent in all its other compounds. It is strictly a non-metallic element.

Occurrence.—Silicon, unlike carbon, is not found in the free condition. In combination it is the most plentiful element after oxygen, and constitutes more than one-quarter of the crust of the earth. The oxide is silica or sand (SiO_2), and this oxide and its compounds are components of many rocks. In the inorganic world silicon is the characteristic element to almost as great an extent as is carbon in the organic realm.

Preparation of Silicon.—When finely powdered magnesium and excess sand are mixed, and one part of the mass is heated, a violent action spreads rapidly through the whole:

$$2Mg + SiO_2 \rightarrow Si + 2MgO.$$

Some magnesium silicide Mg_2Si is formed also. The mixture is treated with a dilute acid which decomposes the magnesium oxide and the silicide, and leaves the **silicon (amorphous)** undissolved. The element is now manufactured at Niagara Falls and elsewhere, by heating sand (SiO_2) with coke in an electric furnace. The process closely resembles that for making carborundum (p. 563), except that less coke is used:

$$2C + SiO_2 \rightarrow 2CO\uparrow + Si.$$

Silicon, as prepared in this way, is a gray, **crystalline** material, **Ferrosilicon** (an alloy of iron and silicon) is made in the same manner by including ferric oxide in the mixture.

Properties. — Amorphous silicon is a brown powder. It unites with fluorine at the ordinary temperature, with chlorine at 430°, with bromine at 500°, with oxygen at 400°, with sulphur at 600°, with nitrogen at about 1000°, and with carbon and boron at temperatures attainable only in the electric furnace. It is dissolved by a mixture of hydrofluoric acid and nitric acid, giving silicon tetrafluoride. **Crystallized silicon** forms needles belonging to the hexagonal system. Silicon and ferrosilicon act readily upon a cold solution of sodium hydroxide (see p. 136), the ortho- or meta-silicate of sodium being formed:

$$Si + 2NaOH + H_2O \rightarrow Na_2SiO_3 + 2H_2 \uparrow .$$

This is one of the sources of hydrogen for filling balloons and airships. A layer of petroleum on the surface prevents frothing. **Hydrogenite** is a mixture of ferrosilicon and dry sodium hydroxide, to which water is added drop by drop. Two kilograms give one cubic meter of hydrogen.

When silicon is heated with fused potassium carbonate, potassium silicate is formed and carbon is liberated. Both kinds of silicon differ from carbon in being fusible at a very high temperature. The product which separates out from the melt on cooling is crystallized silicon.

Silicon Hydride SiH_4. — Silicon resembles carbon in giving many well-defined compounds with hydrogen. The simplest of these, SiH_4, is liberated as a gas by the action of hydrochloric acid upon magnesium silicide:

$$Mg_2Si + 4HCl \rightarrow 2MgCl_2 + SiH_4 \uparrow .$$

The action is similar to that by which hydrogen sulphide is made. Since the magnesium silicide always contains free magnesium, hydrogen is liberated at the same time. By leading the gases through a tube surrounded by liquid air, the silicon hydride is reduced to liquid form, while the hydrogen passes on. The mixture with hydrogen is spontaneously inflammable, like impure phosphine (p. 546), in contact with air. The pure gas becomes so only when its pressure is reduced (compare p. 544). When heated, it decomposes into its constituents.

Silicon Tetrachloride and Tetrafluoride. — The tetrachloride $SiCl_4$ is formed by direct union of the free elements. It is more

conveniently prepared by passing chlorine over a strongly heated mixture of silicon dioxide and carbon:

$$2Cl_2 + SiO_2 + 2C \rightarrow SiCl_4 + 2CO.$$

Chlorine is unable to displace oxygen from combination with silicon, and has, therefore, when alone, no effect upon sand. In the above action, therefore, the carbon is used to secure the oxygen while the chlorine combines with the silicon. This kind of interaction is in some degree different from any which we have hitherto encountered. The principle underlying it was formerly used for making many chlorides (*e.g.*, BCl_3, $AlCl_3$, $CrCl_3$) from oxides, before simple ways of obtaining the elements in the free condition were known.

Silicon tetrachloride is a colorless liquid (b.-p. 59°), which fumes strongly in moist air, and with water precipitates silicic acid (p. 662):

$$SiCl_4 + 4H_2O \rightarrow 4HCl + H_4SiO_4 \downarrow.$$

Mixed vapors of $SiCl_4$, NH_3 and H_2O produce a very dense white *smoke*, consisting of minute particles of NH_4Cl and silicic acid. This smoke was utilized during the war for screening vessels from submarines.

When a concentrated solution of hydrofluoric acid acts upon sand, **silicon tetrafluoride** SiF_4 is liberated:

$$SiO_2 + 4HF \rightarrow 2H_2O + SiF_4.$$

Since the water interacts with the tetrafluoride (see below), the latter is usually made by heating sand with powdered calcium fluoride and excess of concentrated sulphuric acid. In this way the hydrogen fluoride is generated in contact with the sand, and at the same time the sulphuric acid, operating as a dehydrating agent, renders the water inactive. Hydrofluoric acid acts in a corresponding way upon all silicates, whether these are minerals or are artificial silicates like glass (see p. 358).

Silicon tetrafluoride is a colorless gas. It fumes strongly in moist air, and acts vigorously upon water. This interaction is different from that of the tetrachloride, because the excess of the tetrafluoride forms a complex compound with the hydrofluoric acid:

$$3SiF_4 + 4H_2O \rightarrow H_4SiO_4 + 2H_2SiF_6.$$

The silicic acid is precipitated in the water, and may be separated by filtration, leaving a solution of **fluosilicic acid.**

This acid is stable only in solution. When the water is removed by evaporation, silicon tetrafluoride is given off, while most of the hydrogen fluoride remains to the last. Its salts are decomposed in a corresponding way when heated. Fluosilicic acid is used in analysis chiefly because its potassium salt K_2SiF_6 is one of the few salts of this metal which are relatively insoluble in water.

Silicon Dioxide (Silica) SiO_2. — This substance is found in many different forms in nature. In large, transparent, six-sided prisms with pyramidal ends (Fig. 1, p. 6) it is known as **quartz** or **rock crystal.** The ordinary form of quartz (α-quartz) is transformed to an enantiotropic modification (β-quartz) when heated to 575°. X-ray analysis shows that α-quartz is a slightly distorted form of β-quartz, the symmetrical arrangement of the atoms in the lattice of the latter variety being indicated in Fig. 188. Transition

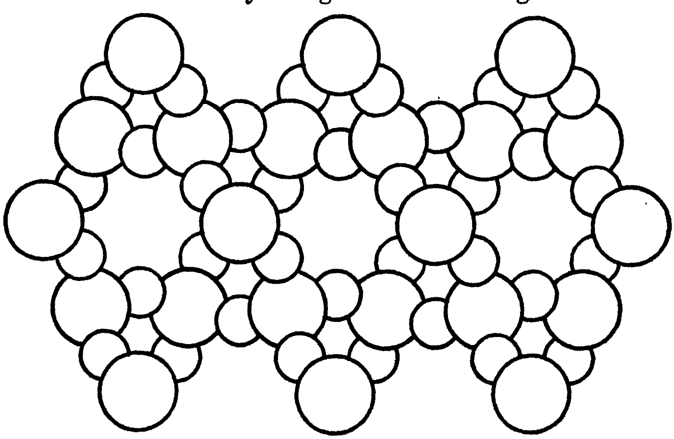


FIG. 188. Structure of β-Quartz.

to other forms (tridymite and cristobalite) also occurs at higher temperatures.

When colored by manganese and iron quartz is called **amethyst,** when by organic matter, **smoky quartz.** Amorphous forms of the same material, often colored brown or red with ferric oxide, are **agate, jasper,** and **onyx,** the last much used in making cameos. Slightly hydrated varieties of silica are the **opal** and **flint.** Forms produced by organisms are **sponges** and **diatomaceous earth** (Kieselguhr or Tripoli powder). The latter is used in scouring materials

and for decolorizing oils and sugar. On account of the tubular form of many of the minute structures of which it is composed, diatomaceous earth can absorb large quantities of liquids. For example, it can take up three times its own weight of nitroglycerine, and is therefore sometimes employed in making dynamite (p. 654).

Silica is found in the hard parts of straw and of bamboo. In the form of whetstones it is used for grinding. Pure **sand** (partly disintegrated quartz) is used in glass manufacture (see p. 664) and in many other industries.

Pure quartz can be melted in the oxyhydrogen blowpipe (at about 1650°), and recently chemical apparatus (**silica ware**) has been made out of it. It has the advantage of being less soluble than glass, and of not breaking even when it is heated white hot and quenched in cold water. Glass breaks when chilled, because the parts first cooled shrink considerably and a great strain is produced. Quartz suffers very little change in volume with change in temperature, and so unequal cooling causes almost no strain. Silica apparatus is more transparent to ultra-violet light than is glass, a property which is utilized in the "quartz mercury lamp."

Silicates. — Silicon dioxide, although differing profoundly from carbon dioxide in its physical nature, nevertheless behaves like the latter chemically. Thus, when boiled with sodium hydroxide solution it forms sodium metasilicate Na_2SiO_3 or orthosilicate Na_4SiO_4 (for nomenclature, see p. 550):

$$SiO_2 + 2NaOH \rightarrow Na_2SiO_3 + H_2O.$$

The salt is left as a gelatinous mass ("water glass") when the water is evaporated. The silicates of sodium and potassium may also be obtained by boiling sand with the carbonates of these metals, or, more rapidly, usually as metasilicates (see p. 664), by *fusing* the mixture:

$$SiO_2 + Na_2CO_3 \rightarrow Na_2SiO_3 + CO_2\uparrow.$$

Water glass or soluble glass, being a salt of a very weak acid with a strong base, gives a solution with an alkaline reaction (p. 408). As manufactured for commercial use, it contains a considerable excess of silica (mainly in colloidal suspension; see p. 641). It is used as a filler in cheap soaps, for fireproofing and waterproofing timber and textiles, as a cement for uniting glass or porcelain, and for preserving eggs.

Silicic Acid H_4SiO_4. — This is an *exceedingly* weak acid. When, therefore, a stronger acid (even carbonic acid will suffice) is added

to a solution of sodium silicate, silicic acid is set free. After a little delay it usually appears as a gelatinous precipitate. If, however, the silicate is poured into excess of hydrochloric acid, no precipitation occurs, the silicic acid remaining in **colloidal suspension.** The precipitate first obtained from either the orthosilicate or the metasilicate approximates in composition to orthosilicic acid H_4SiO_4:

$$Na_4SiO_4 + 4HCl \rightarrow 4NaCl + H_4SiO_4 \downarrow$$
$$Na_2SiO_3 + 2HCl + H_2O \rightarrow 2NaCl + H_4SiO_4 \downarrow,$$

but the gelatinous material, as it dries, only *gradually* loses the elements of water. There seem to be no definite stages, indicating the existence of various acids, such as we observe with phosphoric acid. The final product of drying is the dioxide.

Incompletely dehydrated silicic acid, containing 5–7 per cent of water (**silica gel**), is employed as an adsorbent material for recovering valuable vapors (such as sulphur dioxide, oxides of nitrogen, and volatile organic solvents) from the issuing gases in many large-scale industrial processes. The adsorbed vapors are given up on heating, and the gel is ready for renewed use. Silica gel is also used in deodorizing petroleum oils, and as a catalyst support (p. 420).

Mineral Silicates. — While, in the absence of definite knowledge to the contrary, silicic acid is presumed to be the ortho-acid H_4SiO_4, and no other silicic acids have been made, the salts have been classified mineralogically by imagining them to be derived from various acids representing different degrees of hydration of the dioxide (compare p. 550), or, to put it the other way, different degrees of dehydration of the ortho-acid. The following equations show the relation of the ortho-acid to some of the silicic acids whose salts are most commonly found amongst minerals:

$$H_4SiO_4 - H_2O \rightarrow H_2SiO_3 \ (= SiO_2, H_2O) \quad \text{Metasilicic acid.}$$
$$\left.\begin{array}{l} 2H_4SiO_4 - H_2O \rightarrow H_6Si_2O_7 \ (= 2SiO_2, 3H_2O) \\ 2H_4SiO_4 - 3H_2O \rightarrow H_2Si_2O_5 \ (= 2SiO_2, H_2O) \end{array}\right\} \text{Disilicic acids.}$$
$$3H_4SiO_4 - 4H_2O \rightarrow H_4Si_3O_8 \ (= 3SiO_2, 2H_2O) \quad \text{Trisilicic acid.}$$

Di- and trisilicates are those derived from acids containing two and three units of silicic anhydride, respectively, in the formula. The valences of the negative radicals of the acids are shown by the number of hydrogen units in the formulæ.

The composition of minerals is often exceedingly complex. This is due to the fact that amongst them *mixed salts* are very common, in which the hydrogen of the imaginary acid is displaced by two

or more metals simultaneously. The following list presents in tabular form some **typical or common minerals,** arranged according to the above mentioned classification:

ORTHOSILICATES (H_4SiO_4)		METASILICATES (H_2SiO_3)	
Zircon,	$ZrSiO_4$	Wollastonite,	$CaSiO_3$
Garnet,	$Ca_3Al_2(SiO_4)_3$	Beryl,	$Be_3Al_2(SiO_3)_6$
Mica,	$KH_2Al_3(SiO_4)_3$	Talc (soapstone),	$H_2Mg_3(SiO_3)_4$
Kaolin,	$H_2Al_2(SiO_4)_2,H_2O$	Asbestos,	$Mg_3Ca(SiO_3)_4$
DISILICATE ($H_6Si_2O_7$)		TRISILICATE ($H_4Si_3O_8$)	
Serpentine,	$Mg_3Si_2O_7,2H_2O$	Orthoclase (feldspar),	$KAlSi_3O_8$

Recent X-ray studies of minerals have shown that the old classification described above, while of practical convenience, is theoretically unsatisfactory. The framework of silicates in general consists of linked SiO_4 groups (compare Fig. 188, p. 660). Each silica atom is in the center of a tetrahedron surrounded by four oxygen atoms, but each of these oxygen atoms *may* be common to two neighboring groups. Firmly-bound and continuously extended structures, with varying silicon-oxygen ratios, are thus built up, in which no isolated "complex silicic acid radicals" are distinguishable.

Many minerals consist of solid solutions of two or more simple silicates. Their compositions cannot therefore be represented by any simple formula (see pp. 690-3, 812). Aluminium, it has been found, may either proxy for silicon in the framework, or may act as a cation combined with the framework. This recognition of the dual character of aluminium has made possible the elucidation of many previously puzzling mineral compositions. The structures of the most common minerals, nevertheless, such as quartz, mica and feldspar, represent the simplest ways of linking together tetrahedra.

Garnets are pulverized in manganese-steel crushers and used in making sandpaper. **Mica,** which is obtained in large sheets from Farther India, is used in making lamp-chimneys, for windows in stoves, and as an insulator in electrical apparatus. **Kaolin, or clay,** like mica, is an acid orthosilicate. It is formed in nature as the result of the action of water and carbonic acid upon minerals like feldspar. In such cases, those elements which can form carbonates like potassium, magnesium, and calcium, are usually displaced from combination with the silicic acid. Aluminium, however, is too feeble a base to form a carbonate, and is thus left in combination as silicate. A clay containing lime is called **a marl,** and one containing sand, a **loam.**

Some of these minerals frequently occur mixed together as regular components of certain igneous rocks. Thus, **granite** (p. 6) is a more or less coarse mixture of quartz, mica, and feldspar. Frequently the oblong, flesh-colored or white crystals of the last are large and very conspicuous, both in granite and **porphyry.** In **basalt** the components are usually less easily visible to the eye. **Lava** is the name for any rock recently ejected from a volcano. **Pumice-stone** is the name given to the parts of the lava which are porous, having acquired this texture from the expansion of bubbles of gas consequent upon release of pressure. **Sandstone** is composed of sand cemented together by clay or by calcium carbonate, and colored brown or yellow by ferric oxide.

The hydrated silicates are decomposed by hydrochloric acid, but the others are not affected by acids, or are affected with extreme slowness. Hence special means have to be taken to get the constituents of such minerals into soluble form for the purpose of analysis. Two methods are in use. Sometimes the finely powdered mineral is heated in a platinum dish with hydrofluoric acid until all the silicon has passed off in the form of the tetrafluoride. Since the use of the fluorides would lead to difficulties in the course of the analysis, the resulting mixture of fluorides of the metals is next heated strongly with concentrated sulphuric acid, and the mixture of sulphates thus produced is treated according to the usual routine. In other cases the finely powdered mineral is fused at a bright red heat with a mixture of potassium and sodium carbonates. In this way carbonates of the metals are formed, along with potassium and sodium silicate. Treatment with water dissolves the latter, and leaves the carbonates to be handled in the usual way.

Glass. — Calcium carbonate (limestone) interacts at a high temperature with sand in the same way as does sodium carbonate (p. 661):

$$SiO_2 + CaCO_3 \rightarrow CO_2\uparrow + CaSiO_3$$

giving **calcium silicate.** Now sodium silicate, when alone, is soluble in water. Calcium silicate is insoluble, but forms a brittle, crystalline mass. By using *both* sodium and calcium carbonates, and employing a larger proportion of sand than that shown in the equation, a material is obtained which has the qualities required in glass. When cooled, the molten mass becomes viscous and finally, for all practical purposes, solid. Yet it does not crystallize — it is amorphous. It is also practically insoluble in water.

By pouring the viscous material into molds, or stamping it with dies, articles of *pressed glass* are obtained. Bottles are *blown,* by taking up a sufficient mass of the hot, thick liquid on the end of an iron tube, inserting it in a mold, and blowing until the outline of the

mold is filled. *Window glass* is made by blowing an immense, elongated bubble (6 by 1½ ft.), ripping it while still hot and soft, and flattening it out. *Plate glass* for windows and mirrors is manufactured by pouring out the material upon a cast-iron table, with a raised rim, and passing a large, heated iron roller over it. The plate is subsequently ground flat on both sides and polished with rouge (Fe_2O_3).

Soda-calcium glass is called **soft glass,** because it is easily softened by heating. When potassium carbonate is substituted for sodium carbonate, a less fusible substance, used in making some chemical apparatus, and called **hard glass,** is obtained. When lead oxide is employed in place of the limestone, a potassium-lead silicate is formed which, on being cooled, gives **flint glass.** This glass has a higher density and greater brilliancy than soft glass, and is used in making vessels of cut glass and lamp chimneys.

When glass is allowed to cool quickly, the product is very brittle and apt to crumble to pieces on receiving a shock or scratch. Glassware is therefore all **annealed,** by being passed on a slowly moving frame through a long furnace, which is very hot at the entrance and much cooler at the exit.

Colored glass is made by adding oxides of metals which, with the silica, give colored silicates. Oxide of chromium gives green silicates, oxides of copper and of cobalt blue silicates, and oxide of manganese violet. Gold oxide is reduced to the metal, which remains in colloidal suspension and gives ruby glass. Milky glass is made by adding calcium fluoride, or stannic oxide. The green color of bottle glass is due to iron (ferrous silicate) derived from impure sand or limestone.

The rough surface of **ground glass** is produced with a sand blast. For **engraved glass,** the surface is covered by a stencil to protect it from the sand blast, and only the pattern is left exposed.

In **granite iron ware** the surface is covered with a thin layer of easily fusible glass (enamel, see p. 669).

Pyrex glass, a borosilicate, has also come into extensive use lately for laboratory ware and for cooking vessels. Its low coefficient of expansion renders it much less liable than ordinary glass to crack under sudden temperature changes. Like pure silica, it is very resistant to chemicals. It possesses the further advantage of withstanding much greater mechanical shocks.

Glass is a typical amorphous substance (see p. 62). From the facts that it has no crystalline structure, and that it softens gradually when warmed,

instead of showing a definite melting-point, it is regarded as a supercooled liquid of extreme viscosity. Most single silicates crystallize easily, and have definite freezing- (and melting-) points. Glass may be regarded as a solution of several silicates. When kept for a considerable length of time at a temperature insufficient to render it perfectly fluid, some of its components crystallize out, the glass becomes opaque, and "devitrification" is said to have occurred. The absence of such changes in cold glass may be attributed to that general hampering of all molecular movements and interactions which is characteristic of low temperatures. The word "crystal" popularly applied to glass is thus definitely misleading.

Boron B

As regards **chemical relations,** boron, being a uniformly trivalent element, is a member of the aluminium family (see Table of periodic system, p. 446). Yet it is a pronounced non-metal, and its oxide and hydroxide are acidic: aluminium is a metal, and with its oxide and hydroxide basic properties predominate. Boron and its compounds really resemble carbon and silicon and their compounds in all chemical properties excepting that of valence.

Occurrence. — Like silicon, boron is found in oxygen compounds, namely, in boric acid and its salts. Of the latter, sodium tetraborate $Na_2B_4O_7$, or borax, came first from India under the name of **tincal.** It constitutes a large deposit in Borax Lake in California. **Colemanite,** $Ca_2B_6O_{11},5H_2O$, from California, furnishes a large part of the commercial supply of compounds of boron.

Preparation. — When boric oxide is heated with powdered magnesium: $B_2O_3 + 3Mg \rightarrow 3MgO + 2B$, amorphous boron can be separated with some difficulty from the borides of magnesium in the resulting mixture. When excess of powdered aluminium is used, hard crystals of boron, containing aluminium, are found in the solidified metal. They may be separated by interaction of the metal with dilute hydrochloric acid.

Electrolytic methods have recently been introduced. When fused borax is electrolyzed the sodium liberated at the cathode reduces the borate and gives elementary boron.

Properties. — Amorphous boron is a black powder. It unites with the same elements as does silicon (p. 658), but with somewhat greater activity. Like carbon (pp. 415, 533), it is also oxidized by hot, concentrated sulphuric or nitric acid, the product being

boric acid. The crystalline variety is less rapidly attacked in each case. Both kinds interact with fused potassium hydroxide, giving a borate:

$$2B + 6KOH \rightarrow 2K_3BO_3 + 3H_2.$$

Hydrides and Halides of Boron.—When magnesium boride Mg_3B_2 is treated with hydrochloric acid, a gas containing much hydrogen and several hydrides of boron, notably B_4H_{10} and B_2H_6, is given off.

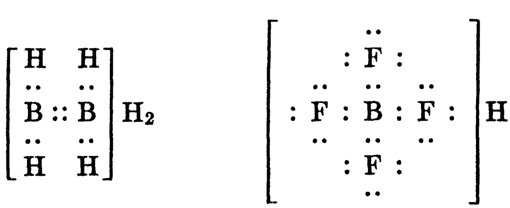
By combined action of carbon and chlorine on boric oxide, using the principle employed in preparing silicon tetrachloride (p. 659), the **trichloride of boron** BCl_3 may be made. It is likewise formed by direct union of the free elements. Boron trichloride is a liquid which boils at 18°, fumes strongly in moist air, and is completely hydrolyzed by water.

Boron trifluoride BF_3 is made by the interaction of calcium fluoride and sulphuric acid with boron trioxide. The mode of preparation and the properties of the substance recall silicon tetrafluoride (p. 659). It interacts with water, like the latter, giving boric acid and **fluoboric acid** HBF_4:

$$4BF_3 + 3H_2O \rightarrow H_3BO_3 + 3HBF_4.$$

The boric acid, not being very soluble, is precipitated. Fluoboric acid is known only in solution, although many of its salts are stable.

The constitution of complex boron compounds is explained by the tendency of the element to assume a co-ordination number of *four* (see p. 527). Thus boroethane B_2H_6 (which has acidic properties) and fluoboric acid HBF_4 may be formulated as follows:



Boric Acid and Boron Trioxide.—Boric acid (boracic acid) H_3BO_3 is somewhat volatile with steam, and is found in Tuscany in jets of water vapor (*soffioni*) which issue from the ground. Water, retained in basins of brickwork, is placed over the open-

ings, and from this water, after evaporation, boric acid is obtained in crystalline form. As boric acid is a very feeble acid, and withal little soluble, it may also be made from sulphuric acid and concentrated borax solution. It crystallizes on cooling the mixture:

$$Na_2B_4O_7 + H_2SO_4 + 5H_2O \leftrightarrows Na_2SO_4 + 4H_3BO_3 \downarrow.$$

Boric acid crystallizes from water in thin white plates, which are unctuous (like graphite and talc) to the touch. It is often added to talcum powder to prevent infection of irritated skin. Its solubility in water is 4 parts in 100 at 18°, and 34 in 100 at 100°. The solution scarcely affects litmus. The green tint it confers on the Bunsen flame is used as a **test** for the acid. At 100° the acid slowly loses water, leaving **metaboric acid** HBO_2, and at 140° **tetraboric acid** is formed: $4HBO_2 \rightarrow H_2B_4O_7 + H_2O$. Strong heating gives the **trioxide** B_2O_3, a glassy, white solid. When dissolved in water, all these dehydrated compounds revert to orthoboric acid H_3BO_3. The solution of boric acid in water is used as an antiseptic in medicine (half-saturated, 2 per cent solution), and sometimes as a preservative for milk and other foods.

Borates. — Borates derived from orthoboric acid are practically unknown. The most familiar salt is **borax** or **sodium tetraborate,** which is usually marketed as the decahydrate $Na_2B_4O_7,10H_2O$. In Germany, borax is prepared from boracite $MgCl_2,2Mg_3B_8O_{15}$, found at Stassfurt, by decomposing a solution of the mineral with hydrochloric acid. The boric acid precipitated is dissolved in boiling water, and sodium carbonate is added: $4H_3BO_3 + Na_2CO_3 \rightarrow Na_2B_4O_7 + 6H_2O + CO_2$. In California it is made from colemanite by interaction with sodium carbonate.

Since boric acid is a feeble acid, borax is hydrolyzed by water, and the solution has a marked alkaline reaction (see p. 408).

When heated with oxides of metals, sodium tetraborate behaves like sodium metaphosphate (see p. 554), and is used in the form of **beads** in analysis. If its formula be written $2NaBO_2,B_2O_3$ it will be seen that a considerable excess of the acid anhydride is contained in it, and that, therefore, a mixed metaborate may be formed by union with some basic oxide. Thus, with a trace of cupric oxide, the bead is tinged with blue, from the presence of a compound like $2NaBO_2,Cu(BO_2)_2$. Cobalt compounds give a deep-blue color to the bead. For the same reason, borax is used in hard soldering. The hard solder (brass) is placed, with a little borax, upon the joint

between the objects of copper or brass which are to be soldered. At the temperature produced by the blast-lamp the borax dissolves the superficial coating of oxides, and the molten solder is able to "wet" the clean surfaces. In welding iron, borax is scattered on the parts, and combines with the oxide to form a fusible mixed borate, which is forced out by the pressure. A substance used thus, to bring infusible bodies into a fusible form of combination, is called a **flux.** Borax is also mixed with glass in making **enamels** for cooking utensils.

Sodium perborate $NaBO_3,4H_2O$ is much used as a bleaching agent and disinfectant in commerce. It can be obtained by the interaction of sodium metaborate and sodium peroxide in solution, but electrolytic methods (*e.g.*, the electrolysis of a well-cooled solution of borax and sodium carbonate) are now favored.

Nitride and Carbide. — One of the difficulties in making free boron is due to its very great affinity for nitrogen, with which, when heated in the air, it unites to form a **nitride** BN. This compound is more easily made by heating borax with ammonium chloride:

$$Na_2B_4O_7 + 4NH_4Cl \rightarrow 4BN + 2NaCl + 7H_2O + 2HCl.$$

The nitride is a white solid which is easily decomposed when heated in a current of steam (compare p. 505): $BN + 3H_2O \rightarrow H_3BO_3 + NH_3$.

A **carbide of boron** B_6C is made by heating the free substances in the electric furnace. It is harder than carborundum, and stands next to the diamond in respect to hardness.

Exercises. — 1. Compare and contrast the elements carbon and silicon, and their corresponding compounds.

2. What product is obtained by the action of hydrochloric acid on magnesium silicide Mg_2Si (compare p. 580)?

3. Derive the valences of zirconium and of beryllium from the formulæ on p. 663.

4. Compare and contrast the elements boron and silicon, and their corresponding oxygen acids.

5. The inside surface of a bottle containing concentrated sodium hydroxide solution becomes etched and dull. To what is this due?

6. Write an equation for the action of heat upon borax.

7. What weight of silicon will be required to give, by interaction with excess of caustic soda solution, sufficient hydrogen to fill a balloon with a capacity of 10,000 cubic feet at 20° and 780 mm.?

8. What is the percentage composition of fluosilicic acid? This substance used to be called hydrofluosilicic acid. Justify the change of name.

9. Devise two distinct ways of demonstrating that silicic acid is an *exceedingly* weak acid (pp. 661–2).

10. Calculate the empirical formulæ of the following minerals from their percentage compositions:

I		II	
SiO_2	73.11	SiO_2	69.00
BeO	10.62	Al_2O_3	19.43
Na_2O	12.24	CaO	0.20
H_2O	3.79	Na_2O	11.47

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CHAPTER XL

PRACTICAL REVIEW OF THE NON-METALLIC ELEMENTS

In the chapters preceding we have classified our substances under one of the particular elements they contained. Thus, chloroform, alcohol, and ether were put under carbon. Hydrogen sulphide and sulphuric acid were considered as compounds of sulphur. Now this classification is of a *theoretical* nature. That chloroform, alcohol, and ether all contain carbon cannot be told by mere *inspection.* We have to make experiments, and to reason about the results, before we reach this inference. Thus we put our *inference* as the title of the chapter, and distributed the observations and data through it. There is, however, another way of classifying the facts, which is just the opposite of this one. It is the *practical* classification. When we obtain a specimen, or when a substance appears in the course of an experiment, we must be able to tell what particular substance it is. If it is a white powder, it may contain almost any of the whole list of elements. It may be any one of several thousands of substances. We can recognize it only by its physical properties (p. 9) and by the physical properties of other substances that we can get from it by interaction with known chemical compounds. We need, therefore, a plan of operation, and this plan must be based upon a *classification by physical properties,* not by constituents.

One benefit of the discussion of such a plan is that it will afford us a *review* of some of the facts already mentioned, by presenting the same facts from a different view-point, and by showing the uses to which they may be put. To avoid unnecessary repetition, we shall refer frequently to the previous statements of the facts. To understand what is here said, therefore, the reader should look up every reference and re-read the statement.

Is the Material a Mixture? — The first question that occurs to us is, whether the material is a single substance or a mixture. When it is a mixture, we can often, though not always, very quickly find this out.

If it is **a solid mass or powder,** we examine it with the naked *eye* and with the help of a *lens.* If we see two or more kinds of particles, as in granite (p. 6), in a mixture of sand and sugar, or in a piece of rusty iron, then it presumably is a mixture.

Whether it appears to the eye to be a mixture, or not, we can next try a *solvent,* such as water, ether, or carbon tetrachloride. If a part of a small sample refuses to dissolve (*e.g.,* sand), while the rest dissolves (*e.g.,* sugar), we have shown that there are two different sets of physical properties, and therefore two different substances (p. 8) present. As there may be very little of the soluble substance in the mixture, we may not perceive at once that anything has dissolved. So we allow a drop of the liquid to evaporate on a clean watch crystal, and observe whether any residue remains.

If the material is **a liquid,** we depend largely on differences in the *volatility* of different substances to find out whether it is a mixture. If a drop evaporates on a watch crystal, leaving a residue (solid or liquid) which does not evaporate, then it is a mixture. If this test fails, because all, or none, evaporates, then we must distil the liquid, with the bulb and most of the stem of a thermometer in the vapor (Fig. 11, p. 30), and note whether the whole comes over at one temperature (single substance, in most cases) or whether the temperature changes as the distillation proceeds (mixture, such as petroleum, p. 579).

These are simply a few examples intended to show how, when a practical problem is before us for solution, we use *physical properties* as the basis of our reasoning and classification.

The Recognition of a Single Substance. — The majority of the substances we have met with are acids, bases, or salts. In identifying a substance of one of these classes, it is convenient to attempt the recognition of the positive and of the negative radicals (or ions) as *two almost separate problems.* In other words, we investigate one radical at a time. On the other hand, substances which do not belong to any of these classes, such as simple substances (sulphur, carbon, chlorine, etc.), oxides (sulphur dioxide, carbon monoxide, etc.), and many organic substances (*e.g.,* carbon disulphide, ethyl alcohol), are investigated as a single problem.

In discussing the recognition of a single substance we shall, for the present, limit ourselves to the non-metallic elements. We shall consider the elementary substances themselves (sulphur, oxygen, etc.), the oxides of such ele-

ments, the few organic compounds described, the *more common* non-metallic negative ions, and ammonium-ion. We shall leave out of consideration until later (Chapter LIII) the metallic elements. We shall also ignore the metallic positive radicals, although one of these (or hydrogen-ion) must inevitably be combined with the negative radical under consideration.

External Examination (Solids).—The specimen may be a solid, a liquid, or a gas. We should note in which of these states it exists under room conditions. What follows applies only to *solids* —the liquids and gases will be taken up later.

Without training in crystallography we can tell little about the **crystalline form** (p. 60) of the specimen. But anything conspicuous, such as **needle**-shape or **cubical** formation of the particles, must be noted.

The **color,** if any, is significant. If **yellow,** the specimen may be *sulphur* (p. 399), if **black,** *carbon* (p. 559), if **black** and crystalline, with **violet** vapor, *iodine* (p. 350). Most substances are colorless.

The **odor,** if any, must be noted. Many salts of ammonium (carbonate, sulphide, etc.) smell of *ammonia* (p. 709). Some sulphides (of sodium, potassium, ammonium, etc.) smell of *hydrogen sulphide* (p. 409). Some acetates smell of *acetic acid* and hypochlorites of *hypochlorous acid* (p. 375).* Some chlorides (*e.g.,* PCl_5 and $AlCl_3$), in moist air, give *hydrogen chloride,* with the odor and fumes characteristic of that substance.

Effect of Heating (Solids).—A great deal may be learned by heating as much of the specimens as will fill the rounded bottom of a small, dry test-tube.

The substance may **fuse.** Many substances, such as some chlorides and most hydrates, do so. Continue heating.

A **sublimate** (solid deposit on the cold part of the tube) may appear. **Black** crystals (from violet vapor) are *iodine:* **white** crystals, with the limitations we have set, show the substance to be a *salt of ammonium* (p. 514). Confirm by smelling, and by adding sodium hydroxide to the original substance (p. 515).

A reddish-brown liquid condenses, becoming, when cold, a yellow solid. This is probably *sulphur* from a *sulphide* (such as FeS_2, p. 396).

Water condenses from *hydrates, acid salts,* and some *organic* compounds. Test the water with litmus paper. An **acid** reaction

* Many experimental details, essential for the successful performance by a beginner of the tests described in this chapter, are here omitted. They will be found in the Author's *Laboratory Outline of Smith's College Chemistry.*

indicates an *acid salt* (p. 418), an easily hydrolyzed salt (*e.g.*, $FeCl_3,6H_2O$), or an *organic acid.* Continue heating, inclining the tube mouth downwards, removing condensed water with filter paper until no more comes off, and heat the residue.

A **gas** is given off. The gas may be **violet** (some *iodides*) or **brown** (some *nitrates*, p. 527, and some *bromides*). If brown, lower a glass rod dipped in silver nitrate solution into the gas in the tube. Bromine will give a cream-colored precipitate (AgBr, p. 348). In case of a negative result try the test for nitrates (p. 524).

The gas may be **colorless.** If it has an **odor,** it may be ammonia from a *salt of ammonium,* sulphur dioxide from a *bisulphite* (p. 418) or from oxidation of a *sulphide* (p. 414). A stifling odor with **fumes** may be sulphur trioxide from some *sulphates* or decomposition products from some *organic* matters.

The gas is **colorless** and **odorless.** It may be oxygen (test with long, glowing splinter of wood) from a *peroxide, chlorate,* or *nitrate* (of K or Na). To learn which of these it is, dissolve or suspend a little of the substance in water, add dilute sulphuric acid, and test for hydrogen peroxide (p. 370). In case of a negative result examine the residue (as on p. 675).

A **colorless, odorless** gas may be carbon dioxide, coming from a *bicarbonate* or a *carbonate.* Lower a glass rod dipped in limewater into the gas in the test-tube (white precipitate, $CaCO_3\downarrow$). It may also be nitrogen from *ammonium nitrite,* or nitrous oxide from *ammonium nitrate* (tests, p. 676).

The substance **carbonizes or chars** and gives an odor of smoldering wood or burning flesh. The compound is *organic.* Identify by properties (pp. 582-3).

Heating may produce **no effect.** On the other hand, *more than one* of these effects (*e.g.*, both water and sulphur dioxide from a bisulphite) may be given by the same specimen.

If heating produces any effect, continue heating until all change ceases, and preserve the residue for later examination.

Effect of Sulphuric Acid on Solids. — Fill the rounded bottom (only) of a test-tube with the substance, add just enough concentrated sulphuric acid to moisten the sample, and warm slightly.

A **gas** (effervescence) which fumes in the breath may be given off. If the gas is **brown** or **yellow,** it may be bromine (bleaches litmus paper) mixed with hydrogen bromide from a bromide (p. 347). It may be nitrogen tetroxide (odor) from a *nitrate*

(p. 522). If **violet,** with brown deposit, accompanied by an **odor** of hydrogen sulphide, it is iodine from an *iodide* (p. 352).

If the gas fumes, but is **colorless,** it may be hydrogen chloride from a *chloride* (add manganese dioxide to get chlorine, p. 241). It may be hydrogen fluoride from a *fluoride* (a moistened glass rod held in the gas acquires a white precipitate of silicic acid, produced by decomposition of silicon fluoride, p. 659).

The gas **does not fume.** If **yellow** it may be chlorine from *bleaching powder* (p. 374) or nitrous anhydride from a *nitrite* (p. 535). A *chlorate* also gives a yellow gas (chlorine dioxide ClO_2) when heated with concentrated sulphuric acid. In this case oxygen will have been obtained in the test on page 674. Heat very carefully, since chlorine dioxide is explosive (stop heating when material in tube begins to crackle!).

The gas does not fume and is **colorless.** An **odor of sulphur dioxide** indicates a *sulphite* (p. 415). An **odor of hydrogen sulphide** indicates a *sulphide.* If the gas is odorless, it may be carbon monoxide (burns, leaving carbon dioxide) from a formate (p. 568), or oxygen from some *oxides* or a *peroxide,* or carbon dioxide from a *carbonate.*

No **gas** evolved indicates a *silicate* (p. 661), *sulphate* (p. 429), *phosphate* (p. 553), or a basic *oxide.*

Sulphuric Acid on the Residue from Pp. 673-4. — If the substance gave off oxygen when heated alone (p. 674), add a drop or two of concentrated sulphuric acid to the residue. If the specimen now gives a yellow gas (nitrous anhydride), the original substance was a *nitrate* (of K or Na), from which the nitrite was formed by heating (p. 535). If it gives a **colorless, fuming** gas (HCl), the original substance was a chlorate (p. 91).

Examination of a Liquid. — Test the specimen with litmus **paper.** A **marked acid reaction** may be due to a solution of an *acid,* an *acid salt* (p. 291), or a hydrolyzed *salt of a weak base* (p. 408).

If it **bleaches** litmus paper, it may be *chlorine-water* or *bromine-water* (odor).

If it is markedly **alkaline** in reaction, it may be a solution of a *base,* a *basic salt* (p. 291), or a hydrolyzed *salt of a weak acid* (p. 408).

Note the **odor.** Ammonium hydroxide, hydrogen sulphide solution, sulphurous acid, concentrated nitric acid and concentrated

halogen acids all have odors. Alcohol, acetic acid, carbon disulphide, carbon tetrachloride, and hydrocarbons (*e.g.*, benzene) have odors easily distinguished from those of the foregoing.

Evaporate a few drops to dryness on a watch crystal. A solid residue shows that the original substance was a *solution* in water (or possibly alcohol or some other solvent, if the vapor has an odor indicating this). If there is a solid residue, a quantity of it may be obtained by evaporating a larger amount of the liquid, and may then be treated as a solid (pp. 673–5).

If the specimen leaves **no residue,** and is not acid or alkaline but has an **odor,** it may be one of the volatile organic compounds named above. If it is **odorless,** it may be a solution of hydrogen peroxide (p. 368) or simply pure water.

Examination of a Gas. — The gas has a **color.** A **brown** gas may be *bromine* or *nitrogen tetroxide.* The former liberates iodine from potassium iodide solution (p. 354), but not bromine from a bromide (insert rods moistened with solution of an iodide and a bromide). The latter becomes deeper brown on warming (p. 527). A **greenish-yellow** gas is *chlorine.* It bleaches, and displaces bromine from a solution of a bromide (p. 349).

The gas may **become colored** (yellow or brown) on admitting air. It is *nitric oxide* (p. 524).

The gas may have a distinctive **odor.** *Sulphur dioxide, hydrogen sulphide, nitrogen tetroxide* and *ammonia* are of this kind.

The gas may **fume** in the breath. The *chloride, bromide,* and *iodide* of *hydrogen* do so. Distinguish by dissolving in a little water and adding manganese dioxide.

The gas may be **combustible.** Burning with a **blue flame** indicates *hydrogen* (vessel bedewed with moisture), or carbon *monoxide* (leaving carbon dioxide, test, p. 567). Burning with a slightly **luminous flame** indicates *methane* (p. 587) and a very luminous flame (often depositing carbon) indicates *ethylene* (p. 585) or *acetylene* (p. 586).

The gas may **relight a glowing splinter of wood.** This is *oxygen,* or *nitrous oxide* (p. 537). The former, with nitric oxide, gives a brown gas (p. 524), the latter does not.

The gas may give a white precipitate ($CaCO_3$) with limewater. This is *carbon dioxide.*

The gas having **none** of these properties is *nitrogen* (p. 505).

In most cases other distinctive properties will be found on the pages referred to.

Exercises. — 1. Look up the references, and give the properties (physical as well as chemical), other than those mentioned on p. 673, by which you should recognize: (*a*) sulphur, (*b*) carbon, and (*c*) iodine.

2. Same question in regard to: (*a*) ammonia, (*b*) hydrogen sulphide, and (*c*) hypochlorous acid.

3. Same question in regard to: (*a*) an acid salt, (*b*) a hydrate, (*c*) nitrogen tetroxide, (*d*) bromine, (*e*) sulphur trioxide, (*f*) hydrogen peroxide, (*g*) ammonium nitrate, (*h*) carbon dioxide.

4. Same question in regard to (pp. 674–5): (*a*) a bromide, (*b*) an iodide, (*c*) a nitrate, (*d*) bleaching powder, (*e*) sulphur dioxide, (*f*) carbon monoxide, (*g*) a silicate, (*h*) a sulphate, and (*i*) a phosphate.

5. Same question in regard to (pp. 675–6): (*a*) conc. and (*b*) dil. sulphuric acid, (*c*) conc. and (*d*) dil. nitric acid, (*e*) conc. and (*f*) dil. hydrochloric acid, (*g*) hydrobromic acid, (*h*) hydriodic acid, (*i*) phosphoric acid, (*j*) sulphurous acid.

6. Same question in regard to: (*a*) chlorine-water, (*b*) alcohol, (*c*) acetic acid, (*d*) carbon disulphide, (*e*) carbon tetrachloride, (*f*) a hydrocarbon.

7. Same question in regard to: (*a*) nitric oxide, (*b*) hydrogen, (*c*) methane, (*d*) ethylene, (*e*) acetylene, (*f*) nitrous oxide, (*g*) ozone, (*h*) nitrogen.

8. Why does sodium sulphide smell of H_2S (see pp. 408–9)?

9. When ammonium nitrate is heated in a test-tube, the gases evolved do not relight a glowing splinter at all readily. How can this be reconciled with p. 537?

CHAPTER XLI

THE METALLIC ELEMENTS

In developing the chemistry of the metallic elements, we shall naturally take as much advantage as possible of the *classification of the metals into families* as given in the table of the Periodic System on p. 446. The consideration of each family separately will enable us to bring out very clearly the outstanding similarities in chemical behavior of the various elements comprised in it, the gradations in their properties and in the properties of their compounds, and the occasional lapses of the more original members from the family standards.

In some cases we shall find these lapses so serious that it becomes necessary to disregard the periodic arrangement altogether, and to utilize other methods of grouping the elements. The main defects in the periodic system have already been noted (p. 449), and the reader should pay particular attention, at this point, to the possibility of employing the *activity order of the metals,* in which many features in the behavior of metals and their compounds are summed up, as an alternative means of classification.

Before we take up any particular group of the metals in detail, however, a preliminary survey of the characteristic properties of the whole community will be of value. A knowledge of the physical properties of the metals is, to the chemist, of the greatest importance in connection with their manufacture and treatment. The following brief statement in regard to some of these properties is illustrative rather than exhaustive. It should be noticed that the properties of a metal vary somewhat according as the specimen has been prepared by rolling, casting, or some other process. Numerical values, therefore, when given, are only approximate.

Physical Properties of the Metals. — Metals show what is commonly called a **metallic luster,** but, as a rule, they do so only when in compact form. Magnesium and aluminium exhibit it when powdered, but in this condition most metals appear black.

In compact masses the metals are usually silvery white in color. Gold and copper, which are yellow and red respectively, are the conspicuous exceptions.

The metals can all be obtained in **crystallized form,** when a fused mass is allowed to cool slowly and the unsolidified portion is poured off. In almost all cases the crystals belong to the regular system (see p. 60). With the metals most nearly allied to the non-metals, however, they do not. Thus, the crystals of antimony and bismuth belong to the hexagonal system, and those of tin to the square prismatic.

The metals vary in **specific gravity** from lithium, which is little more than half as heavy as water (sp. gr. 0.53), to osmium, whose specific gravity is 22.5. Those which have a specific gravity less than 5 are called the **light metals,** and the others the **heavy metals.**

Most metals are **malleable,** and can be beaten into thin sheets without loss of continuity. Those which are allied to the non-metals, however, such as arsenic, antimony, and bismuth, are brittle. The order of the more important elements in respect to this property, beginning with the most malleable, is: Au, Ag, Cu, Sn, Pt, Pb, Zn, Fe, Ni.

The **tenacity** of the metals places them in an order different from the above. It is measured by the number of kilograms which a piece of the metal 1 sq. mm. in section can sustain without breaking. Some values are as follows: Fe 62, Cu 42, Pt 34, Ag 29, Au 27, Al 20, Zn 5, Pb 2.

The **hardness** is measured by the ease with which the material may be scratched by a sharp, hard instrument (see Appendix II). Potassium is as soft as wax, while chromium is hard enough to cut glass.

The **temperature** at which the metal **fuses** has an important bearing on its manufacture. Most of the following **melting-points** of pure metals are taken from the International Critical Tables (1926):

Mercury	−39°	Zinc	419°	Cast iron	1150°
Potassium	62°	Antimony	630°	Manganese	1260°
Sodium	97°	Magnesium	651°	Nickel	1452°
Tin	232°	Aluminium	660°	Iron (pure)	1535°
Bismuth	271°	Silver	960°	Chromium	1615°
Cadmium	321°	Gold	1063°	Platinum	1755°
Lead	327°	Copper	1083°	Tungsten	3370°

The methods of manufacture and the treatment of metals are much influenced also by their **volatility.** The following are easily distilled: Mercury, b.-p. 357°; potassium, b.-p. 760°; cadmium,

b.-p. 767°; sodium, b.-p. 880°; zinc, b.-p. 907°. Even the most involatile metals can be vaporized in the electric arc.

The good **conductivity** of metals for **electricity** distinguishes them with some degree of sharpness from the non-metals. They show considerable variation amongst themselves, silver conducting sixty times as well as mercury. The conductivity increases as the temperature is lowered, and this fact is taken advantage of in the measurement of the temperature of liquefied gases. The **platinum resistance thermometer** consists chiefly of a wire of platinum. The resistance of this metal diminishes so rapidly, with decreasing temperature, that measurement of its resistance can be used for the accurate determination of the temperature. Near the absolute zero of temperature, metals exhibit only infinitesimal resistance.

The resistance at 0° of a column of mercury 1 sq. mm. in section and 1.063 meters long is the practical unit, and is called one ohm. The following table gives the specific conductivities of the metals, expressed in terms of the number of meters of wire 1 sq. mm. in section which, at 18°, offer a resistance of one ohm:

Copper, annealed	62.9	Platinum	9.1
Silver, 99%	60.2	Nickel, 97%	8.5
Copper, drawn	56.2	Iron (0.1% C)	8.3
Gold	41.3	Steel (0.1% C)	5.0
Aluminium, 99%	34.0	Lead	4.8
Zinc, pure	16.4	Mercury	1.05
Brass (70% Cu, 30% Zn)	15.1	Bismuth	0.84

To compare these **conductivities** with those of solutions, it may be said that decinormal hydrochloric acid (p. 323) has a specific conductivity on the above scale of 0.035, or a thirtieth of that of mercury. Metallic conduction of electricity is due entirely to the **transfer of electrons through the material**; *there is no decomposition as in the case of solutions.*

The metals are also, in general, good **conductors of heat.** Silver, copper and aluminium, in the order named, possess the highest values for this property.

General Chemical Relations of the Metallic Elements. — Since most of the compounds of the metals are strong electrolytes, their aqueous solutions, except when the metal is a part of a compound ion, all contain the metal in the ionic state, and the resulting substances, such as potassium-ion and cupric-ion, have constant properties, irrespective of the nature of the negative ion with which they may be mixed. The properties of the ions, simple and compound,

are much used in making tests in analytical chemistry. On the other hand, the chemical properties of the oxides and of the salts in the *crystalline state* are of importance in connection with metallurgy.

There are **three chemical relations** which are **characteristic of the metallic elements.** All of them have already been discussed somewhat fully.

1. The metals are able by themselves to form *positive* radicals of salts, and therefore to exist alone as positive ions (pp. 147, 440).

2. The oxides and hydroxides of the metals are **basic** (pp. 174, 235).

3. Each *typical* metal forms compounds with the halogens which, in the presence of excess of the corresponding halogen acid, are not extensively (often not even appreciably) hydrolyzed by water. The same thing is true of other compounds of the metals with negative radicals derived from active acids, such as the nitrates or sulphates.

In reference to the third characteristic, the **non-hydrolysis of halides of typical metals,** a word of explanation is required. **Strong bases** (hydroxides of typical metals), such as sodium hydroxide, give, with **feeble acids,** salts whose solutions are **alkaline in reaction.** This is due, as we have already explained (p. 408), to partial hydrolysis. In the same way, **weak bases,** in other words the hydroxides of less active metallic elements, give, with **strong acids,** salts whose solutions are not neutral, but **acid in reaction.** Thus cupric chloride solution is feebly acid, since cupric hydroxide is a very weak base:

$$\begin{array}{c} Cu^{++} + 2Cl^- \\ 2H_2O \rightleftarrows 2OH^- + 2H^+ \\ \downarrow\uparrow \\ Cu(OH)_2 \end{array}$$

Where hydrolysis is appreciable and the base formed is only very slightly soluble, as in the case of aluminium chloride, the reaction tends to go forward continuously through precipitation of the hydroxide. Accumulation of hydrogen-ion in the solution, however, acts as a counterbalancing factor diminishing hydroxyl-ion concentration and preventing complete hydrolysis. Any hydroxide precipitated, indeed, may always be brought back into solution by addition of a concentrated solution of the active acid involved.

The halogen compounds of typical non-metals, on the other hand, such as PCl_3 and $SiCl_4$, are *completely decomposed by water* (see pp. 231, 659), and the hydrolysis cannot in such instances be reversed, however great a concentration of the halogen acid is added. The hydroxide produced is here itself acidic, such as H_3PO_3, H_4SiO_4. That the line between metals and non-metals is not perfectly distinct, nevertheless, may be seen by reference to the case of tellurium (p. 439). Other examples of elements on the borderline between metals and non-metals will be met with later in the arsenic family Chapter L).

Salts formed by the interaction of *strong* bases with *strong* acids exhibit, as has already been explained (p. 406), no signs of hydrolysis in aqueous solution. With salts derived from a base and an acid, both of which are weak, however, the extent of hydrolysis is inevitably very considerable. If either the resulting acid or the resulting base is insoluble, hydrolysis will go on to completion. Aluminium carbonate and ammonium silicate are examples.

Other Chemical Relations of the Metals. — There are **three other chemical relations** which are **shown by many metallic elements,** but no one of them applies to all.

1. An oxide or hydroxide which is basic may also be acidic, as, for example, zinc hydroxide (p. 748). Even when this is not the case, some other oxide of the metal may be acidic exclusively, as is manganese heptoxide (p. 891). In consequence of either of these facts, a metal may form *part* of the negative radical of a simple salt, and therefore be found in a negative ion, as, $ZnO_2^{=}$ or MnO_4^-.

2. Some salts of certain metals combine with those of others to give complex salts (see p. 686). Of this sort are the complex cyanides, such as $K.Ag(CN)_2$ and $K_4.Fe(CN)_6$. A metal thus forms part of the negative radical of a salt of a complex acid, and therefore is found in an *anion* like $Ag(CN)_2^-$ or $PtCl_6^{=}$.

3. Some metals also form parts of complex cations which are contained in solutions of molecular compounds (p. 524). Thus, when $AgCl,3NH_3$ is dissolved in water, or when ammonium hydroxide is added to a solution of a salt of silver, the positive ion is found to be $Ag(NH_3)_2^+$ (see also p. 788).

Occurrence of the Metals in Nature. — The minerals from which metals are extracted are known as **ores.** They present a comparatively small number of different kinds of compounds. Most of the metals are found in more than one of these forms, so that in the following statement the same metal frequently occurs more than once.

When the metal occurs free in nature, it is said to be **native.** Thus we have gold, silver, the platinum family, copper, mercury, bismuth, antimony, and arsenic occurring native (see p. 143).

The metals whose **oxides** are important minerals are iron, manganese, tin, zinc, copper, and aluminium. The metals are obtained commercially from the oxides in each of these cases.

The metals whose **sulphides** are used as ores are iron, nickel, cobalt, antimony, lead, cadmium, zinc, copper, and mercury.

From the **carbonates** we obtain iron, lead, zinc, and copper. Several other metals, such as manganese, magnesium, barium, stron-

tium, and calcium occur in larger or smaller quantities in the same form of combination.

The metals which occur as **sulphates** are those whose sulphates are not freely soluble, namely lead, barium, strontium, and calcium.

Compounds of metals with the **halogens** are not so numerous. Silver chloride furnishes a limited amount of silver. Sodium, potassium and magnesium chlorides are found in the salt-beds, and cryolite $3NaF,AlF_3$ is used in the manufacture of aluminium.

The natural **silicates** are very numerous, but are seldom used for the preparation of the metals. Many of them are employed for other commercial purposes, kaolin (p. 663) or clay being a conspicuous example of this class.

Methods of Extraction from the Ores. — The art of extracting metals from their ores is called **metallurgy.** Where the metal is **native,** the process is simple, since melting away from the accompanying matrix or **gangue** is all that is required. Frequently a **flux** is added. A flux (p. 669) is a substance which interacts with infusible materials to give fusible ones. It combines with the gangue, giving a fusible **slag** (resembling glass). Since the slag is a melted salt, usually a silicate, and does not mix at all with the molten metal, separation of the products is easily effected. When the ore is a *compound,* the metal has to be liberated by our furnishing a material capable of combining with the other constituent. The details of the process depend on various circumstances. Thus the volatile metals, like zinc and mercury, are driven off in the form of vapor, and secured by condensation. The involatile metals, like copper and iron, run to the bottom of the furnace and are tapped off.

Where the ore is an **oxide** it is usually reduced by heating with carbon in some form. This holds for the oxides of iron and copper. Some oxides are not reducible by carbon in an ordinary furnace. Such are the oxides of calcium, strontium, barium, magnesium, aluminium, and the members of the chromium group. At the temperature of the electric furnace even these may be reduced, but the carbides are formed under such circumstances, and the metals are more easily obtained otherwise. Recently, heating the pulverized oxide with finely powdered aluminium has come into use, particularly for operations on a small scale. Iron oxide is easily reduced by this means, and even the metals manganese and chromium may be liberated from their oxides quite readily by this action. On

account of the great amounts of heat liberated, this procedure has received the name **aluminothermy** (see p. 770).

When the ore is a **carbonate,** it is first heated strongly to drive out the carbon dioxide (see p. 564): $FeCO_3 \rightleftarrows FeO + CO_2 \uparrow$, and then the oxide is treated according to one of the above mentioned methods. When the ore is a **sulphide,** it has to be calcined (p. 414), in order to remove the sulphur, and the resulting oxide is then reduced.

Chlorides and **fluorides** of the metals can be decomposed by heating with metallic sodium. This method was formerly employed in the making of magnesium and aluminium.

The metals which are not readily secured in any of the above ways can be obtained easily by **electrolysis** of the fused chloride or of some other compound. Aluminium is now manufactured entirely by the electrolysis of a solution of aluminium oxide in molten cryolite.

Compounds of the Metals: Oxides and Hydroxides. — The **oxides** may be made by direct burning of the metal, by heating the nitrates (see p. 527), the carbonates (see p. 564), or the hydroxides (see p. 131). Most oxides are practically insoluble in water, but those of the metals of the alkalies (p. 696) and alkaline earths (p. 720) interact with water rapidly to give the hydroxides. Oxides are usually stable. Those of gold, platinum, mercury, and silver decompose readily when heated, but as we go up the electromotive series of the metals (p. 313), the difficulty of decomposing their oxides by heat rapidly increases (see p. 143). The metals, like the non-metals, frequently give several different oxides. Those of the univalent metals (having the form K_2O), if we leave cuprous oxide and aurous oxide out of account, have the most strongly basic qualities. Those of the bivalent metals of the form MgO are also predominantly base-forming. Those of the trivalent metals of the form Al_2O_3, known as **sesquioxides** (Latin, *sesqui,* one-half more), are the least basic of the basic oxides. The oxides of the forms SnO_2, Sb_2O_5, CrO_3, and Mn_2O_7, in which the metals have valences from 4 to 7, are mainly acid-forming oxides, although the same elements usually have other lower oxides, which are basic.

The **hydroxides** are formed, in the cases of the metals of the alkalies and alkaline earths, by direct union of water with the oxides. The majority may be produced more readily by double decomposition, when a soluble hydroxide acts upon a salt (see p. 234). All hydroxides, except those of the alkali metals, lose the elements

of water when heated, and the oxide remains. In some cases the loss takes place by stages, just as was the case with orthophosphoric acid (p. 551). Thus lead hydroxide $Pb(OH)_2$ first gives the hydroxide $Pb_2O(OH)_2$, then $Pb_3O_2(OH)_2$, and then the oxide PbO. The hydroxides of mercury and silver are evidently unstable, for, when the precipitate obtained by adding a soluble hydroxide to one of their soluble salts is dried, it is found to contain nothing but the corresponding oxide. With the exception of those of the metals of the alkalies and alkaline earths, the hydroxides are all very little soluble in water.

Compounds of the Metals: Salts. — In the succeeding chapters we shall describe only those salts which are manufactured commercially, or are of special interest for some other reason. The various salts will be described under each metal. Here, however, a few remarks may be made about the characteristics of the more common groups of salts.

The **chlorides** may be made by the direct union of chlorine with the metal (see p. 243), or by the combined action of carbon and chlorine upon the oxide (see p. 659). The general methods for making any salt (p. 290), such as the interaction of a metal with an acid, or of the oxide, hydroxide, or another salt with an acid, or the double decomposition of two salts, may be used also for making chlorides. The chlorides are for the most part soluble in water. Silver chloride, mercurous chloride, and cuprous chloride are almost insoluble, however, and lead chloride is not very soluble. Most of the chlorides of metals dissolve without appreciable decomposition, but hydrolysis is conspicuous in the case of the chlorides of the trivalent metals, such as aluminium chloride and ferric chloride (see p. 684). The chlorides of some of the bivalent metals (magnesium, calcium and zinc) are slightly hydrolyzed also, but, as a rule, only when they are heated with water. Most of the chlorides are stable when heated, but those of the noble metals, particularly gold and platinum, are decomposed, and chlorine escapes. The chlorides are usually the most volatile of the salts of a given metal, and so are preferred for the production of the spectrum (p. 706) of the metal, and for fixing the atomic weight of the metal by use of the vapor density. Some metals, for example iron, form two or more different chlorides.

The **sulphides** are formed by the direct union of the metal with sulphur, or by the action of hydrogen sulphide or of some soluble sulphide upon a solution of a salt (see p. 411). In one or two cases

they are made by the reduction of the sulphate with carbon. The sulphides, except those of the alkali metals, are but little soluble in water. The sulphides of aluminium and chromium are hydrolyzed completely by water, giving the hydroxides, and those of the alkali metals and the metals of the alkaline earths are partially hydrolyzed (see p. 409).

The **carbides** are usually formed in the electric furnace by interaction of an oxide with carbon (see p. 563). Some of them are decomposed by contact with water, after the manner of calcium carbide, giving a hydroxide and a hydrocarbon. Of this class are barium carbide BaC_2, aluminium carbide Al_4C_3, and manganese carbide MnC. Others, such as those of molybdenum Mo_2C and chromium Cr_3C_2, are not affected by water.

The **nitrates** may be made by any of the methods used for preparing salts. They are *all* at least fairly soluble in water.

The **sulphates** are made by the methods used for making salts, and in some cases by the oxidation of sulphides. They are all soluble in water, with the exception of those of lead, barium, and strontium. Calcium sulphate is meagerly soluble.

The **carbonates** are prepared by the methods used for making salts. They are all insoluble in water, with the exception of those of sodium and potassium. The hydroxides of aluminium and tin are so feebly basic that they do not form stable carbonates (see p. 663).

The **phosphates** and **silicates** are prepared by the methods used in making salts. The former are obtained also by special processes already described (p. 553). With the exception of the salts of sodium and potassium, all the salts of both these classes are insoluble.

Salts of Complex Acids. — These salts are of many classes, and arise by direct union of two salts. Thus we have cyanides like potassium argenticyanide $K.Ag(CN)_2$, potassium cuprocyanide $K.Cu(CN)_2$, and potassium ferrocyanide $K_4.Fe(CN)_6$:

$$K.CN + AgCN \rightarrow K.Ag(CN)_2.$$

The complex sulphur compounds of arsenic, antimony, and tin, such as sodium sulphostannate $Na_2.SnS_3$, are made in the same way:

$$Na_2S + SnS_2 \rightleftarrows Na_2.SnS_3.$$

Many double halides are of a like nature, as potassium chloroplatinate $K_2.PtCl_6$, chloroplatinic acid $H_2.PtCl_6$, and sodium chloraurate $Na.AuCl_4$. In every case, the metal of one of the original salts is contained in the negative radical (the anion). Fluosilicic acid (p. 660) is a compound analogous to those of the last group, excepting that SiF_4 from which it is formed, is not a salt, and silicon is not a metal.

The characteristic of these compounds is that, when they are ionized, the less positive metal is contained in a complex anion like $Ag(CN)_2^-$, $SnS_3^=$, $PtCl_6^=$. In fact, they behave, in most respects, like ordinary single salts. Thus, they undergo double decomposition in the normal manner, the complex ion acting as a whole. For example, a soluble ferrocyanide with a zinc salt gives zinc ferrocyanide:

$$K_4.Fe(CN)_6 + 2ZnSO_4 \rightleftarrows Zn_2.Fe(CN)_6 \downarrow + 2K_2SO_4.$$

This behavior distinguishes salts of complex acids from double salts (p. 291). In typical cases the latter resemble the former, indeed, only in their mode of preparation (by union of two simple salts), and in solution are resolved once more into the component salts and their separate ions. The distinction must be regarded, however, only as a means of rough classification for practical purposes (compare p. 525). In reality, all complex ions give at least a trace of the simpler ions, and many are decomposed to a noticeable extent. At the other extreme, some double salts form complex ions in appreciable amounts in concentrated solutions.

In harmony with the above characteristic, salts of complex acids, like potassium ferrocyanide, when treated with acids, like sulphuric acid, undergo double decomposition, and give the free complex acid (here ferrocyanic acid):

$$K_4.Fe(CN)_6 + 2H_2SO_4 \rightleftarrows H_4.Fe(CN)_6 \downarrow + 2K_2SO_4.$$

But in many cases the acids are unstable, those of the cyanides, for example, giving up hydrocyanic acid and those of the complex sulphur compounds giving hydrogen sulphide:

$$H_2.SnS_3 \leftrightarrows H_2S \uparrow + SnS_2 \downarrow .$$

The complex halogen acids, however, like $H_2.PtCl_6$ and $H.AuCl_4$, are stable, and are fairly active as acids.

The similarity of these compounds to oxygen acids, and their salts, may be seen if we imagine them to be cases in which cyanogen, sulphur, chlorine, and other radicals have taken the place of oxygen in the anion. Thus, $[(CN)_2]^{II}$, $[Cl_2]^{II}$, and S^{II} are equivalent to O^{II}. Many of the corresponding oxygen compounds are actually known, as sodium stannate Na_2SnO_3 and sodium aurate $NaAuO_2$, corresponding respectively to $Na_2.SnS_3$ and $Na.AuCl_4$.

The behavior of complex ions is discussed further under Copper (p. 788).

Solubility of Bases and Salts. — The solubilities of a few salts at various temperatures have already been given (p. 205). For the **exact solubilities** of a large number of **bases and salts** at 18°, see the **Table inside the cover,** at the front of this book. Each square contains two numbers expressing the solubility of the compound whose cation stands at the head of the column and whose anion is indicated at the side. The solubility is that of the hydrate stable at 18°, where such exists. The **upper number** in each case gives the number of grams of the anhydrous salt held in solution by 100 c.c. of water. The **lower number** shows the number of moles in 1 l. of the saturated solution, and indicates therefore the concentration in terms of a molar solution as unity — the molar solubility. In the cases of the less soluble compounds the values are not exact, but they will serve to show roughly the relative solubilities when several substances are compared. The numbers for small solubilities have been abbreviated. Thus, $0.0_64 = 0.0000004$.

It will be seen that some compounds, like zinc chloride and barium iodide, are exceedingly soluble; that others, like potassium chloride and barium chlorate, are of medium solubility; that still others, like calcium hydroxide and calcium sulphate, are sparingly soluble; and, finally, that some, like calcium oxalate CaC_2O_4 and barium chromate, are almost insoluble. The reader should note the fact, however, that the differences in solubility even amongst the insoluble salts are as great as amongst the soluble ones.

Solubilities at different temperatures are shown in the **diagram,** Fig. 87, p. 206.

Hydrated Forms of Salts Commonly Used. — In the following table, the figures refer to the number of molecules of water in the hydrates which are deposited by aqueous solutions of the salts in the neighborhood of 18°. The letter *h* means that the compound is stable when *heated,* the letter *a* that it is not affected by the *air,* the letter *d* that the salt is *deliquescent,* and the letter *e* that the hydrate loses water spontaneously in an open vessel, *i.e.,* is *efflorescent.*

Composition of Stable Hydrates of Salts. 18°

	K	Na	Li	Ag	Ba	Sr	Ca	Mg	Zn	Cd	Cu	Pb
Cl	0*h*	0*h*	2*a*	0*h*	2*a*	6*e*	6*d*	6*d*	1½*d*	2½*e*	2*d*	0*h*
Br	0*h*	0*h*	0*h*	0*h*	2*a*	6*d*	6*d*	6*d*	2*d*	4*e*	4*e*	0*h*
I	0*h*	0*h*	0*h*	0*h*	2*d*	6*d*	0*d*	8*d*	0*d*	0*a*	..	0*h*
NO_3	0*a*	0*a*	0*d*	0*a*	0*a*	4*e*	4*d*	6*d*	6*d*	4*d*	6*d*	0*a*
ClO_3	0*a*	0*a*	0*d*	0*a*	1*a*	5*d*	2*d*	6*d*	6*d*	2*d*	6*d*	1*a*
BrO_3	0*a*	0*a*	0*d*	0*a*	1*a*	1*a*	1*a*	6*e*	6*a*	2*a*	6*a*	1*a*
IO_3	0*a*	3*e*	0*d*	0*a*	1*a*	6*e*	6*e*	4*a*	2*a*	0*a*	1*a*	0*a*
$C_2H_3O_2$	0*d*	3*e*	2*d*	0*a*	1*a*	½*a*	2*d*	4*d*	3*a*	3*d*	1*a*	3*a*
SO_4	0*h*	10*e*	0*h*	0*a*	0*h*	0*h*	2*a*	7*e*	7*e*	2⅔*a*	5*a*	0*h*
CrO_4	0*h*	10*e*	2*a*	0*a*	0*h*	0*h*	1*a*	7*e*	..	..	..	0*h*
C_2O_4	1*a*	0*a*	0*a*	0*a*	1*a*	0*a*	1*a*	2*a*	2*a*	3*a*	1*a*	0*a*
CO_3	1½*d*	10*e*	0*a*	0*e*	0*h*	0*h*	0*a*	3*e*	0*a*	0*a*	..	0*a*

The measurement of the vapor tension of hydrates in the course of dehydration (see p. 176) gives definite information in regard to whether there are other hydrates, say of cupric sulphate, with less than than the normal number of formula-weights of water. If there were only two substances, $CuSO_4$ and $CuSO_4,5H_2O$, with no compound of intermediate composition, then a partially decomposed specimen would be made up partly of the one substance and partly of the other. But if there were an intermediate compound, say $CuSO_4,3H_2O$, then desiccating a specimen of the pentahydrate would give nothing but mixtures of $CuSO_4,3H_2O$ and $CuSO_4,5H_2O$ until all the latter was decomposed. Then, and only then, the trihydrate would begin to lose water. Now the trihydrate, being a definite and different substance, would have a vapor tension of its own under such conditions, and experimental study would show its presence.

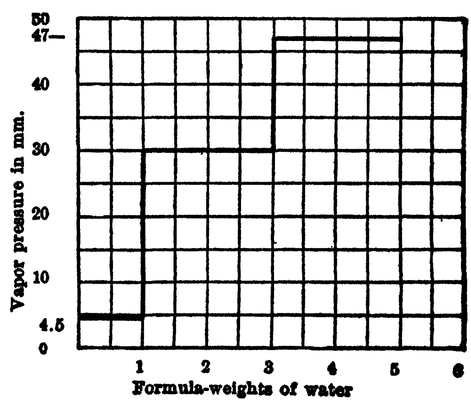


FIG. 189. Vapor Pressure Equilibria in the System: $CuSO_4 - H_2O$.

Experiment shows that there really are three hydrated cupric sulphates. The introduction of crystals of the pentahydrate into the barometric vacuum (Fig. 80), at 50°, results in a vapor tension of 47 mm., and this vapor tension is observed so long as any pentahydrate remains to be decomposed. But if the free space above the mercury is enlarged considerably, so that the withdrawal of water vapor into it reduces the proportion in the crystals below that represented by the formula $CuSO_4,3H_2O$ (or, as may be effected more readily experimentally, if crystals already dehydrated to the composition $CuSO_4,3H_2O$ are employed), the vapor tension suddenly drops to 30 mm. As the desiccation continues, this tension is main-

tained until the composition has reached $CuSO_4,H_2O$. At this point the vapor pressure falls to that of the monohydrate in process of dehydration, 4.5 mm., and remains at this value until all the rest of the water has been removed. Had there been no intermediate compound with $3H_2O$ the tension would have dropped at once from 47 mm. to 4.5 mm. If, conversely, we try to combine water as vapor with anhydrous cupric sulphate, at 50°, a vapor pressure of at least 4.5 mm. is required to cause union to take place. The union stops when one formula-weight of water has undergone combination. To introduce more, the concentration of the water vapor must be increased to nearly seven times its first value, namely, to 30 mm. pressure. This enforces combination up to $CuSO_4,3H_2O$. For further hydration, a still higher pressure of water vapor is needed (47 mm.), and the absorption ceases when $CuSO_4,5H_2O$ has been formed.

There are thus three distinct reversible actions which succeed one another as the hydration proceeds:

$$CuSO_4 + H_2O \rightleftarrows CuSO_4,H_2O.$$
$$CuSO_4,H_2O + 2H_2O \rightleftarrows CuSO_4,3H_2O.$$
$$CuSO_4,3H_2O + 2H_2O \rightleftarrows CuSO_4,5H_2O.$$

The graphic representation of these facts (Fig. 189) will make the behavior of the compounds clearer. The proportion of water combined with one formula-weight of cupric sulphate is laid off along the horizontal axis. The pressures at which it enters or leaves the compounds at 50° are the ordinates. As far as $1H_2O$ the pressure is constant (4.5 mm.). Beyond that point and up to $3H_2O$ it is constant but much higher. Between $3H_2O$ and $5H_2O$ it is constant again but higher still.

The above discussion shows that the last formula-weight of water, in hydrates which dissociate by stages, is not different in kind from the others. It differs only in the degree of tenacity with which it is held. It is therefore unnecessary, merely on this account, to dignify it by the separate and misleading name of *water of constitution,* as has been done by some chemists.

Isomorphism.—All substances which crystallize in one of the forms belonging to the regular system (p. 60) must necessarily have identical crystalline shapes. Thus, crystallized specimens of sodium chloride and of lead sulphide (galena) in their natural shapes are cubical. The forms found in other systems, however, are capable of assuming an infinite diversity of shapes. The relative lengthening or shortening in one direction, shown by the square prismatic and hexagonal forms (p. 60), for example, makes it possible for each separate substance to adopt proportions which are more or less different from those of every other substance. Each substance, not belonging to the regular system, does, in fact, crystallize invariably in forms based upon its own fundamental proportions, and differs therefore in its angles from all other such substances in a way that is clearly recognizable by refined measurement.

Now it is found that substances which are chemically somewhat similar (see below) frequently crystallize in the same system and show proportions which are almost, although not quite, identical. Further, two or more such substances, when the approach to identity in angles is not accidental, can take part in the construction of one and the same crystal. A crystal of one such substance placed in a solution of the other will continue to grow, and in doing so will follow the pattern already set, and simply increase in dimensions by accretion of the new material. When a solution containing two such substances deposits crystals, the structures are, not some of them of one material and some of the other, but all are made up of *both* in a ratio determined by the relative amounts of the substances in the solution.* **Substances** related in these two ways, that is, **having, when separate, crystalline forms which are closely alike and being capable of forming homogeneous crystals containing varying proportions of the two ingredients,** are called **isomorphous substances** (Greek ἴσος, equal; μορφή form). Thus, potassium permanganate $KMnO_4$ and potassium perchlorate $KClO_4$ crystallize in the rhombic system, forming crystals with very similar angles (Fig. 23, p. 61), and when a solution containing both is allowed to evaporate there is formed but one set of crystals made up of both substances. Similarly, potassium iodide and ammonium iodide crystallize in cubes of the regular system and, since all cubes are alike, necessarily show absolutely identical angles. In addition to this, however, they crystallize together from a solution containing both salts. Other pairs from amongst substances belonging to the regular system would not necessarily do this. These two salts are therefore isomorphous. Substances which thus form *mixed crystals* have approximately equal molecular volumes (see p. 693).

In the course of our study of the compounds of the metals we shall have occasion to note many examples of isomorphism. Thus the heptahydrates of the sulphates of many of the bivalent metals, such as $ZnSO_4,7H_2O$, $NiSO_4,7H_2O$, $MgSO_4,7H_2O$, etc., belong to the rhombic system, and form an isomorphous set of substances known as the *vitriols* (p. 749).

The alums (p. 774) also constitute an important set, and crystallize, separately and together, in the regular system. Amongst minerals, lead sulphide PbS and silver sulphide Ag_2S form a common

* In general, two substances which are absolutely unrelated may be deposited simultaneously from mixed aqueous solutions, but some of the crystals are *pure* specimens of one substance and the rest are *pure* specimens of the other.

isomorphous pair, and nearly all natural specimens of galena (p. 829) contain at least a little silver sulphide.

The chemical significance of isomorphism was at first exaggerated. Thus the elements magnesium and iron are not especially similar in their chemical relations, excepting that both are bivalent; yet they form several pairs of compounds which, like the sulphates (p. 691), are isomorphous. Still, in practical chemical work a knowledge of the relations of a substance in respect to isomorphism is indispensable. It enables us to predict the probable impurities in a homogeneous-looking material, for non-isomorphous substances would have given a heterogeneous mixture with it. It assists us in separating and purifying chemical substances, for non-isomorphous substances can be separated by recrystallization from water (p. 385), or by washing with water or some other solvent at a temperature at which the solubilities of the substances are different (see Potassium nitrate, p. 702). Isomorphous substances, however, can be separated only by conversion into some other form of combination in which the property is lacking.

When we consider isomorphism not from the standpoint of external crystal form, but from that of internal lattice structure (p. 64), we see that two things are necessary for two substances to give homogeneous "mixed crystals," or, more correctly, **solid solutions.** The first is that they shall, in the pure state, crystallize in the same fundamental pattern; in other words, the arrangement of their constituent atoms in the lattice must be similar. In order for this to hold, it was formerly thought that groups of similar valence must be present, and the law of Mitscherlich was postulated: *Isomorphous substances have similar chemical formulæ.*

This is, indeed, frequently true, as will be evident from the examples given above, and the rule has proved of service historically in suggesting the valence of new elements. A much more general and useful principle, however, has recently superseded it. It was pointed out by Langmuir, in the development of the octet theory (p. 488), that "there is one property, namely crystalline form, which should depend on the arrangement of the electrons in substances rather than upon the magnitude of the forces between their atoms." Now the arrangement of the external electrons in the constituent atoms of polar compounds does *not* depend on valence. The ion F^- which has gained one electron and the ion $O^=$ which has gained two electrons have the same general electron arrangement, as also have the ion Na^+ which has lost one electron and the ion Mg^{++} which has lost two. Some non-polar substances also, according to the octet theory (see co-valence, p. 489), have identical electron arrangements. Nitrogen N_2 and carbon monoxide CO may be quoted as examples. Langmuir called such ions and substances **isosteres**, and the validity of his prediction that isosteric compounds should be isomorphous may be seen from the following typical pairs of substances which are miscible in the crystalline state: NaF-MgO; MgF_2-Na_2O; KCl-CaS; $CaCl_2$-K_2S; $NaNO_3$-$CaCO_3$;

$KClO_4$-$SrSO_4$; $NaHSO_4$-$CaHPO_4$. The list could be extended almost indefinitely.

There is however a second condition which must be satisfied for two substances to be perfectly miscible *in all proportions* in the solid state. Not only must they possess a similar lattice structure, but the *dimensions* of the unit cell in the two cases must be very close together. Only when this condition is fulfilled can the various atoms or groups of atoms replace each other indiscriminately in the lattice and build up a stable structure over the entire range of composition. This is the case, for example, with copper and nickel. When the cell dimensions do vary significantly, solid solution may still occur, but it is limited in its extent. The introduction of a different radical here results in a strain in the original structure, which increases until a saturated solution of one substance in the other is obtained, and beyond this point a homogeneous mixture is unstable. As examples of this type, showing only partial miscibility in the solid state, lithium chloride and silver chloride may be cited.

Alloys. — In many cases metals dissolve readily in one another in the fused state, and when cooled form **alloys.** Alloys are of several types. In the first place, the metals may remain completely dissolved in one another in the solid state. An example is afforded by copper and manganese. A perfectly homogeneous alloy, however, may also be obtained in other ways. If a liquid mixture is suddenly cooled ("quenched") it may exist indefinitely, like glass, in a super-cooled amorphous condition, being still, strictly speaking, a liquid. *Hard steel* (essentially a solution of about 1% carbon in iron) is partially of this class. A third case in which a homogeneous alloy results is when exactly the necessary proportions of the two metals are taken to form a stable compound. Many such compounds are known, copper and magnesium for example giving the two compounds CuMg and Cu_2Mg, melting at 570° and 897° respectively.

The majority of alloys, nevertheless, although they may appear uniform to the eye, are heterogeneous in character, and when a polished surface is etched by a suitable chemical and examined under the microscope, the differences in crystal structure of the various components present are immediately evident. Most molten mixtures of metals deposit one component first on cooling, and only when the concentration of the other component has been considerably increased and the temperature considerably lowered does the second component begin to crystallize out as well (see Fig. 190). We thus obtain crystals of one metal imbedded in a **matrix,** or mother deposit, of another. If the metals are incompletely miscible in the solid state at low temperatures, or if metals that

form compounds are taken in irregular proportions, substantially the same state of affairs is established.

In gray *cast iron* we have a very clear case of a heterogeneous alloy, tiny particles of carbon having separated out from the iron. *Babbitt metal* (Sb 3, Zn 69, As 4, Pb 5, Sn 19 per cent) and other **anti-friction alloys** (or **bearing metals**) give, on cooling, a mass in general soft, but containing hard particles. The latter bear most

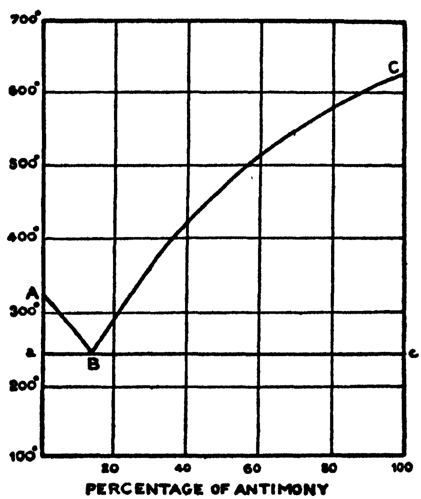


FIG. 190. Lead-Antimony Diagram.

Pure lead melts at 326°; pure antimony at 632°. The freezing-point of each metal is lowered on addition of the other, as expressed by the curves AB and CB respectively. These curves represent *temperatures of initial crystallization.* As the crystallization proceeds, the percentage of the second component in the residual liquid steadily increases, and the final freezing-point of all mixtures is given by B — *the eutectic point* of the system — at 245° and 13 per cent Sb. Conversely, the temperature of *initial fusion* of all mixtures is represented by the line ac. the first liquid forming invariably having the composition B, and complete liquefaction being attained only when the appropriate point on the curve AB or CB is reached.

of the pressure, yet, as the alloy wears, they are pressed into the softer matrix so that a smooth surface is always presented. An alloy with the opposite composition, a hard mass containing softer particles, would develop heat by friction much more rapidly.

The properties of alloys, especially when compounds are formed, may be markedly different from the properties of their constituent elements. Thus the nickel alloy used in coins contains 75 per cent of copper and only 25 per cent of nickel, yet it shows none of the color of the former metal. The conductivity of *manganin* for electricity, on the scale used in the table on p. 680,

is only 2.3, although it contains 84 per cent of copper to 4 of nickel and 12 of manganese. This alloy is used for wire resistances.

In subsequent chapters we shall take up many examples of alloys which are of great commercial value because of the elimination of certain very undesirable properties, or the introduction of certain highly desirable properties, which has resulted through the addition of a suitable proportion of one metal to another.

Alloys in which *mercury* is one of the components are known as **amalgams,** and are formed with especial ease by the lighter metals. Of the common metals, iron is the least miscible with mercury.

Exercises. — 1. What do we mean by saying that an oxide is strongly or feebly basic, or that it is acidic?

2. What is meant by the same terms when applied to an hydroxide?

3. Compare the molar solubilities at 18°, (*a*) of the halides of silver, and (*b*) of the carbonates and (*c*) oxalates of the metals of the alkaline earths, noting the relation between solubility and atomic weight.

4. What is the molar concentration of chloride-ion in saturated solutions of silver chloride and lead chloride at 18°, assuming complete ionization in these very dilute solutions?

5. Formulate, by means of ionic equations, the hydrolysis of ammonium sulphide $(NH_4)_2S$. Will a solution of this *neutral* salt exhibit an acid or an alkaline reaction (refer to table on p. 317)?

6. Why does not the precipitate of silicic acid obtained when ammonium silicate is dissolved in water redissolve when concentrated ammonia is added to the solution (compare p. 681)?

7. What metallic characteristics do the following elements possess: hydrogen, iodine, tellurium? Why do we, nevertheless, class them among the nonmetals?

8. Write the formulæ of six *neutral salts* which will dissolve in water to give solutions with an acid reaction, and of six which will dissolve in water to give solutions with an alkaline reaction.

9. Write the formulæ of six salts which, in spite of very extensive hydrolysis, will give aqueous solutions with a reaction approximately neutral.

10. How could you show that the two alloys of copper and magnesium, alluded to on p. 693, are definite compounds and not just mixtures?

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CHAPTER XLII

THE ALKALI METALS

The metals of this family form a homogeneous group, and there is a very general similarity between the properties of the corresponding compounds. Some of the physical properties of the elements themselves can best be shown in tabular form.

	At. No.	At. Wt.	Sp. Gr.	M.-P.	B.-P.
Lithium Li.........	3	6.94	0.53	186°	1400°
Sodium Na.........	11	23.00	0.97	97.5°	880°
Potassium K.......	19	39.10	0.86	62.5°	760°
Rubidium Rb......	37	85.44	1.53	38.5°	700°
Caesium Cs........	55	132.91	1.90	26.5°	670°

It will be seen that the specific gravities of the elements increase with rising atomic weight, while the melting-points and boiling-points fall (compare p. 445). A table including all the physical properties, both of the elements and their compounds, would show similar characteristics in a general way, with here and there noticeable irregularities such as that shown by the specific gravity of sodium. For example, the melting-points of the hydroxides are: lithium, 450°, sodium 318.4°, potassium 380°, rubidium 301°, caesium 272.3°. Sodium (m.-p. 97.5°) and potassium (m.-p. 62.5°) give together an alloy which is *liquid* at room temperature (p. 693).

The Chemical Relations of the Alkali Metals. — Reference to the electromotive series of the metals (p. 313) will show that the metals which are chemically most active are included in this group. A freshly cut surface of any of these metals tarnishes by oxidation as soon as it is exposed to the air. All of these metals decompose water violently (see p. 129), liberating hydrogen. The hydroxides which are formed by this action are **alkalies** or exceedingly active bases (p. 235). It is from this fact that the family receives its name. In the dry form these hydroxides are not decomposed by heating, while the hydroxides of all other metals lose water more

or less easily. From the periodic classification of the elements (p. 446) it will be seen that the alkali metals all fall into place in the left hand side of the second column. In all their compounds they are **univalent.**

In this family, just as in the halogen family (p. 358), we shall find that although the elements and their corresponding compounds are all very much alike in properties, yet the first member is decidedly irregular in certain respects. Instead of beginning with lithium, therefore, we shall reverse the order of presentation, and start with the elements of higher atomic weight. **Rubidium** and **cæsium** are both extremely rare elements, and their compounds have no particular interest. The first of the alkali metals to come up for discussion is consequently **potassium.**

The compounds of **ammonium** will also be discussed in connection with those of potassium, to which they present the greatest resemblance.

Potassium K

Occurrence. — Silicates containing potassium, such as **feldspar** and **mica** (p. 663), are constant constituents of volcanic rocks, and from the weathering of these rocks, and of the detritus formed from them which constitutes a large part of the soil, the potassium used by plants is obtained. These minerals have not yet been brought into commercial use as sources of potassium compounds. Many salt deposits (see p. 614) contain potassium chloride, alone **(sylvite)** and in combination with other salts, and most of the compounds of potassium are manufactured from this material. Potassium sulphate occurs also in the salt layers.

Potassium salts are all very faintly radioactive, emitting beta-rays. It has been found that the radioactivity is due to a minute trace of an isotope of atomic mass 40, with a half-period of approximately 1×10^{11} years. Salts of rubidium (p. 707) exhibit the same phenomenon.

Preparation. — Potassium was first made by Davy (1807) by bringing the wires from a battery in contact with a piece of moist potassium hydroxide. Globules of the metal appeared at the negative wire. Electrolytic processes have now come back into use commercially, molten potassium chloride being the substance decomposed. Castner's reduction process involves the heating of potassium hydroxide with a spongy mass of carbide of iron. The potassium passes off as vapor, and is condensed:

$$6KOH + 2C \rightarrow 2K_2CO_3 + 3H_2 + 2K.$$

Physical and Chemical Properties. — Potassium is a silver-white metal which melts at 62.3°. It boils at 760°, giving a greenish vapor. The density of the vapor shows a molecular weight of about 40, a slight association of K to K_2 being indicated thereby. The metal and its compounds confer a violet tint upon the Bunsen flame, and the spectrum (p. 706) shows characteristic lines.

The element unites violently with the halogens, sulphur, and oxygen. In consequence of the latter fact it is usually kept under petroleum, an oil which neither contains oxygen itself, nor dissolves a sufficient amount of moisture from the air to permit much oxidation of the potassium to take place. A white, crystalline **hydride** KH is formed when hydrogen is passed over potassium heated to 360°. When thrown into water it gives potassium hydroxide, and the hydrogen is liberated.

Potassium Chloride KCl. — Sea-water and the waters of salt lakes contain a relatively small proportion of potassium compounds. During the evaporation of such waters, however, the potassium compounds tend to accumulate in the mother-liquor while sodium chloride is being deposited. Thus, when the Salt Lake in Utah shall have finally dried up, the *upper* (last to be formed) part of the bed of salts which it will leave behind will contain layers rich in compounds of potassium. This condition is realized in geological deposits which have been formed in the same way. Thus, at Stassfurt, near Magdeburg, there is a thickness of more than a thousand meters of common salt, more or less mixed with and interspersed by layers of sedimentary deposits. Above this, and therefore deposited last, are 25–30 meters of salt layers in which the potassium salts are chiefly found, while over all are several hundred meters of sandstone. Formerly the upper layers were simply stripped off and rejected. Now, however, the revenue obtained from the products of these layers is many times greater than that coming from the rock-salt below.

The isolation of pure potassium chloride from the salt deposits has already been discussed (p. 614), in connection with its use as a fertilizer. It is a white substance crystallizing in cubes, melting at about 770°, and slightly volatile at high temperatures.

The Other Halides of Potassium. — When iodine is heated in a concentrated solution of potassium hydroxide, potassium iodate and **potassium iodide** are both formed (compare p. 384):

$$6KOH + 3I_2 \rightarrow 5KI + KIO_3 + 3H_2O.$$

The dry residue from evaporation is heated with powdered carbon to reduce the iodate, and all the iodide can then be purified by recrystallization. The salt forms large, somewhat opaque cubes. It is used in medicine and for precipitating silver iodide AgI in photography.

The aqueous solution takes up free iodine, forming KI_3, in equilibrium with dissolved iodine: $I^- + I_2$ (dissolved) $\rightleftarrows I_3^-$. It is used in testing for starch, and in reactions in which a solution of free iodine is requred.

Potassium bromide KBr may be made in the same way as the iodide. It crystallizes in cubes. It is used in medicine and for precipitating silver bromide in making photographic plates.

The **fluoride of potassium** KF may be obtained by treating the carbonate or hydroxide with hydrofluoric acid. It is a deliquescent, white salt. When treated with an equimolecular quantity of hydrofluoric acid it forms **potassium-hydrogen fluoride** KHF_2, a white salt which is also very soluble (for its crystal structure, see Fig. 39, p. 71). This acid salt is used in the preparation of pure hydrofluoric acid, since hydrogen fluoride is liberated from it as a vapor at a high temperature.

Potassium chloride is the least soluble of the halides of potassium, the bromide, fluoride, and iodide coming next in that order. The position of the fluoride as the third in order, when we should expect it to be the least soluble (p. 359), shows that this compound is somewhat exceptional. It is also slightly hydrolyzed by water, as if it were a salt of a weak acid (compare p. 317). Besides KHF_2, noted above, other acid fluorides with the formulæ KH_2F_3 and KH_3F_4 have been obtained.

Potassium Hydroxide KOH. — This compound, known also as caustic potash, was formerly made entirely by boiling potassium carbonate with calcium hydroxide suspended in water (milk of lime):

$$\left.\begin{matrix} Ca(OH)_2(\text{solid}) \rightleftarrows 2OH^- + Ca^{++} \\ 2K^+ + CO_3^= \end{matrix}\right\} \rightleftarrows CaCO_3(\text{solid}).$$

The operation is conducted in iron vessels, because porcelain, being composed of silicates, interacts with solutions of bases. On account of the very limited solubility of the calcium hydroxide (0.08 g. in 100 g. water at 100°), the water takes up fresh portions into solution only when the part dissolved has already undergone chemical change. The calcium carbonate which is precipitated is, however, still more insoluble (0.0013 g. in 100 g. water), and hence the action

goes forward. It cannot, nevertheless, for reasons which will be developed later (p. 757), be carried beyond a certain point, and in practice such an amount of water is employed that the solution at no time contains more than about 10 per cent of potassium hydroxide. The conclusion of the action is recognized when a clear sample of the liquid no longer effervesces on addition of a dilute acid, and is therefore free from potassium carbonate. After the precipitate has settled, the potassium hydroxide is obtained by evaporation of the clear liquid.

Potassium hydroxide is now manufactured by electrolytic processes also. Usually a solution of potassium chloride is electrolyzed, the details of the process being as already described for sodium hydroxide in an earlier chapter (p. 233). Besides the **Nelson** cell (Fig. 97), the **Townsend-Baekeland, Briggs,** and **Du Bois** cells are of this type.

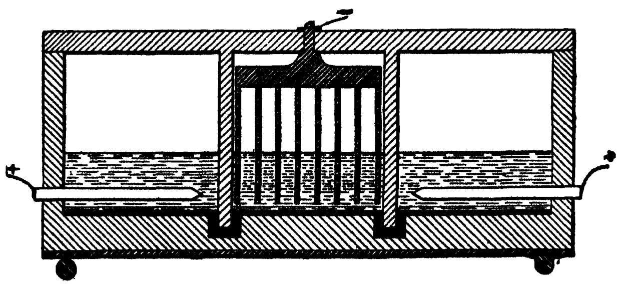


FIG. 191. Castner-Kellner Apparatus for Manufacture of Potassium Hydroxide.

The **Castner-Kellner apparatus** (Fig. 191), which was formerly much used but has now been largely superseded by the above, employs a different principle very ingeniously for the separation of the products. The two end compartments are filled with brine and contain the graphite anodes. The central compartment contains potassium (or sodium) hydroxide solution and the iron cathode. In the end compartments, chlorine is liberated upon the graphite anodes, and is collected for the manufacture of liquefied chlorine or of bleaching powder. The ions of potassium or of sodium, as the case may be, are discharged upon a layer of mercury which covers the whole floor of the box, and the free metal dissolves in the mercury, forming an amalgam (p. 695). The reason why the use of mercury permits the discharge of the metal-ion, making this discharge easier than that of hydrogen-ion, will be developed in detail in a later chapter (Electromotive chemistry,

p. 853). The layer of mercury extends beneath the partitions, and a slight rocking motion given to the cell causes the amalgam to flow to and fro below the partition into the central compartment. Here the alkali metal leaves the amalgam in the form of ions and is attracted to the iron cathode. Upon this, hydrogen from the water ($H_2O \rightleftarrows H^+ + OH^-$) is preferentially discharged, and the residual hydroxyl-ion, together with the metal-ion, gives a continuously increasing yield of potassium or sodium hydroxide in the solution in the central compartment. A slow influx of salt solution into the side cells and a corresponding overflow of the alkaline solution from the central cell are continuously maintained. The overflowing liquid contains 20 per cent of alkali. Since in this form of the apparatus there is no undecomposed chloride present in the part of the solution which contains the hydroxide, simple evaporation to dryness furnishes the solid alkali. The amount of mercury required, however, involves a large investment of capital.

Potassium hydroxide is exceedingly soluble in water, and consequently, instead of being crystallized from solution, the molten residue from evaporation is cast in sticks or granules. The hydroxide is highly deliquescent. It also absorbs carbon dioxide from the air, giving potassium carbonate. Commercially, it is chiefly employed in the making of soft soap.

When, for chemical purposes, the hydroxide is required free from potassium carbonate and other impurities, it is dissolved in alcohol, in which the other substances are not soluble. Evaporation of this solution gives pure caustic potash.

Potassium oxide K_2O may be made by heating potassium nitrate with potassium in a vessel from which air is excluded: $2KNO_3 + 10K \rightarrow 6K_2O + N_2$. It interacts violently with water, giving the hydroxide. When exposed to the air it unites spontaneously with oxygen, and a yellow **peroxide** K_2O_4 is formed. The same peroxide is formed when potassium burns in air or oxygen.

Potassium Chlorate $KClO_3$. — The preparation of this salt by interaction of potassium chloride with calcium chlorate has already been described (p. 384). It is also made by electrolysis of potassium chloride solution, the potassium hydroxide and chlorine which are liberated being precisely the materials required. All that is necessary is to use a warm, concentrated solution and to provide for the mixing of the material generated at the electrodes. The salt crystallizes out when the solution cools.

Potassium chlorate crystallizes in monoclinic plates. It melts at

368°, and at a temperature slightly above this the visible liberation of oxygen begins (see pp. 91, 386). On account of the ease with which its oxygen is liberated, the salt is employed in making fireworks and as a component of the heads of Swedish matches. With acids it is used as an oxidizing agent on account of the chloric acid which is set free (p. 386). It is also employed in medicine as a gargle in throat infections.

Potassium Nitrate KNO_3. — The supply of the natural nitrate being insufficient, the salt is made by double decomposition from Chile saltpeter $NaNO_3$:

$$NaNO_3 + KCl \rightarrow KNO_3 + NaCl \downarrow .$$

Sodium chloride is not much more soluble in hot water than in cold. The three other salts, however, become very soluble as the temperature rises (see Fig. 87, p. 206). Hence, when sodium nitrate and potassium chloride are heated with very little water, they dissolve, much sodium chloride is precipitated, and it is chiefly potassium nitrate that remains in solution. The mass is filtered quickly through canvas to separate the precipitate, and potassium nitrate crystallizes from the filtrate as it cools. The crystals are only very slightly contaminated with sodium chloride, for, as the curve shows, common salt is little less soluble at 10° than it is at 100°.

Potassium nitrate gives long prisms belonging to the rhombic system (Fig. 24, p. 61). It melts at about 335°, and when more strongly heated gives off oxygen, leaving potassium nitrite KNO_2. Although it does not form a hydrate, the crystals enclose small portions of the mother-liquor, and consequently contain both water and impurities. When heated, the crystals fly to pieces explosively (**decrepitate**), on account of the vaporization of this water. Many substances which form large crystals, and do not melt when warmed, behave in the same way and for the same reason. In consequence of this, the purest salt is made by violent stirring of the solution during the operation of crystallization, the result being the formation of a crystal-meal.

The salt is used in making gunpowder and fireworks. It is employed also in preserving ham and corned beef.

Gunpowder. — Gunpowder is composed of potassium nitrate (75 per cent), charcoal (15 per cent) and sulphur (10 per cent). The ingredients are moistened with water, and intimately mixed by

grinding under the heavy rollers of a mill. The "mill cake" is then broken up and granulated to the required size.

The explosion results largely from the union of the charcoal with the oxygen from the nitrate, and of the sulphur with the potassium. One gram of powder yields 264 c.c. of gas (CO_2, CO, and N_2) measured at 0° and 760 mm., and a much larger volume at the temperature of the explosion. The chemical reactions involved produce, for each gram of the powder, about 660 calories of heat. The *explosion* is due to the *suddenness* with which the gases are generated and the heat is developed. The smoke is composed of particles of solid (hygroscopic) compounds of potassium and is therefore very slow in dissipating itself (see p. 421). **Smokeless powder** (p. 654) produces no solids when it explodes and has largely displaced gunpowder in recent years. The latter, however, is still extensively used in mining, and for detonating charges of smokeless powder.

Paper saturated with potassium nitrate solution and dried, is known as **touch-paper.** The salt interferes with the access of air to the cellulose, and itself supplies the oxygen for the combustion. The product consequently does not blaze, yet smoulders and cannot be blown out.

Potassium Carbonate K_2CO_3.—This salt is manufactured chiefly from potassium chloride, from the Stassfurt deposits. The chloride is heated with magnesium carbonate (magnesite), water, and carbon dioxide *under pressure:*

$$2KCl + 3MgCO_3 + CO_2 + 5H_2O \rightarrow 2KHMg(CO_3)_2{,}4H_2O + MgCl_2$$

The hydrated double salt separates from the liquid containing the more soluble magnesium chloride and is decomposed by heating with water at 120°. The product is a solution of potassium carbonate, from which the precipitated magnesium carbonate is removed by filtration and used over again. In some districts potassium carbonate is still extracted from wood-ashes, its original source and the origin of its name, **potash.** The sugar beet takes up a considerable amount of potash from the soil, and the extract, after removal of the sugar, is evaporated and calcined. Wool scourings, when evaporated and calcined, also afford a small supply.

This salt is usually sold in the form of an anhydrous powder (m.-p. about 890°). When crystallized from water it gives a hydrate $2K_2CO_3{,}3H_2O$. It is deliquescent. Its aqueous solution has a marked alkaline reaction. The commercial name of the substance is **pearl ash.** It is used in making soft soap and hard (*i.e.,*

difficultly fusible) glass. It is also employed, by interaction with acids, in making other salts of potassium.

Its conversion to the **bicarbonate** $KHCO_3$ in the purification of carbon dioxide has already been mentioned (p. 564).

When a concentrated solution of potassium bicarbonate is electrolyzed in such a way that the anode, towards which the HCO_3^- ions travel, consists of a thin platinum wire, the crowding together of the discharged material results in the formation of the **percarbonate** $K_2C_2O_6$ (compare p. 433). The operation must be conducted between —15° and 0°. When the solution in the porous cell surrounding the anode is evaporated, the product is obtained as an amorphous bluish-white powder. The substance liberates oxygen when heated, and in other respects behaves like the persulphates.

Potassium Cyanide KCN. — This salt, a derivative of the highly poisonous hydrocyanic acid (prussic acid) HCN, is made by heating dry potassium ferrocyanide (see p. 907):

$$K_4Fe(CN)_6 \rightarrow 4KCN + Fe + 2C + N_2.$$

When the residue is extracted with water, only the potassium cyanide dissolves, and it is easily crystallized in pure form from the solution.

Potassium cyanide is extremely soluble in water, and is therefore deliquescent. Its poisonous qualities are equal to those of hydrocyanic acid. A solution of the salt gives an alkaline reaction, showing that hydrocyanic acid is a feeble acid. It is so very feeble, indeed, as to be displaced by other weak acids like carbonic acid (compare p. 374). Hence, since the salt when exposed to the air is always moist, hydrocyanic acid is slowly liberated from it by the action of the carbon dioxide in the atmosphere. The salt consequently exhibits the bitter almond odor of the free acid.

Potassium cyanide has a great tendency to form complex compounds with cyanides of other metals (see p. 686). Complex compounds of this kind are used in the galvanic deposition of silver and gold in commercial electroplating, and are formed when the cyanide is used in extracting gold (p. 812) from its ores.

In most respects the corresponding compounds of potassium and sodium are similar in their physical properties and chemical action. Now for many purposes sodium salts, which are much more abundant and consequently much cheaper, are just as good as the corresponding potassium compounds. Consequently the shortage in potassium salts has been relieved to some extent by educating the industries into substituting compounds of sodium for those of potassium wherever practicable. In some cases the sodium salt has

actually turned out to be *superior* to the potassium salt that it has displaced! Sodium cyanide, for example, is not only less expensive, gram for gram, than potassium cyanide, but one g. mol. wt. (49 g.) of NaCN is just as effective in electroplating, or in gold extracting, as one g. mol. wt. of KCN (65 g.), so that even the quantity required is cut down considerably.

Some compounds of potassium, however, cannot be replaced by sodium salts. Sodium nitrate, for example, cannot be readily substituted for potassium nitrate in explosives, because it is *deliquescent*. Similarly sodium chloride will not function as a fertilizer in place of potassium chloride, since plants insist upon plenty of potassium.

Potassium Sulphate K_2SO_4. — Potassium sulphate is a constituent of several double salts found in the Stassfurt deposits. It is extracted from **schoenite** $MgSO_4,K_2SO_4,6H_2O$ and **kainite** $MgSO_4,MgCl_2,K_2SO_4,6H_2O$. The former is treated with potassium chloride and comparatively little water, whereupon the relatively insoluble potassium sulphate crystallizes out, and the magnesium chloride remains in the mother-liquor. The crystals belong to the rhombic system, contain no "water of crystallization", and melt at 1066°. This salt is employed in preparing alum (see p. 774) and is much used as a **fertilizer.**

The methods of preparation and the properties of other salts of potassium in which sulphur is a constituent, such as the bisulphate, sulphide, sulphite, etc., have been given in sufficient detail in earlier chapters, to which reference should here be made.

Potassium bisulphate is used in analysis for the purpose of interacting with insoluble oxides and silicates and converting them into soluble sulphates. The substance is more efficient than sulphuric acid for this purpose, because the latter cannot be heated above 330°, while the liberation of the active sulphur trioxide from the bisulphate takes place at a bright-red heat.

Properties of Potassium-ion K^+: Analytical Reactions. — The positive ion common to all potassium salts is a colorless substance. It unites with all negative ions, and most of the resulting compounds are fairly soluble. For its **recognition** we add solutions containing those ions which give with it the least soluble salts. Thus, with chloroplatinic acid H_2PtCl_6 it gives a yellow precipitate of potassium chloroplatinate K_2PtCl_6. Since nearly one part of this salt dissolves in 100 parts of water, the test is far from being a delicate one. The solubility in alcohol is much smaller, and consequently the precipitate may frequently be obtained from a dilute solution by adding more than an equal volume of alcohol. Picric acid (p. 654) gives potassium picrate $KOC_6H_2(NO_2)_3$, which is much less soluble

in water (0.4 parts in 100 at 15°). Perchloric acid $HClO_4$ and fluosilicic acid H_2SiF_6 likewise give somewhat insoluble salts of potassium. **Potassium-hydrogen tartrate** $KHC_4H_4O_6$ is precipitated by the addition of tartaric acid to a sufficiently concentrated solution of a potassium salt. The normal tartrate $K_2C_4H_4O_6$ is much more soluble. It may be obtained by treating the precipitate with a solution of potassium hydroxide. Addition of an acid to this solution causes reprecipitation of the bitartrate.

The Spectroscope. — A much more delicate test for the recognition of a potassium compound consists in the examination by means of the **spectroscope** of the light given out by a Bunsen flame, in which a little of the salt is held upon a platinum wire. When the amount of potassium is considerable, and no other substance which would likewise color the flame is present to mask the effect, the violet tint is easily recognizable by the eye. In general, however, the light must be analyzed.

White light is composed of vibrations of every wave-length within a certain range. If the light is made up of a few wave-lengths only, it appears to the eye to be colored. Now, when a narrow bundle of rays of white light, coming through a slit, falls upon a three-sided prism, the rays of various wave-lengths are retarded to different extents as they pass through the glass, and in consequence are bent from their paths by varying amounts. Fig. 192 shows a horizontal section through the slit (*S*) and prism, in which the width of the slit and of the beam of light are exaggerated. The light emerging at the other side of the prism consists, therefore, of a series of images of the slit arranged side by side. The red light is least refracted, and the red images of the slit, therefore, are most nearly in the same straight line with the original beam. The yellow, green, blue, and violet images are displaced more and more from this direction, and the resulting colored band is called a **spectrum.** The whole series of images of the slit may be received upon a screen, or directly upon an eye looking towards the prism. Now, when the light comes from the vapor of a potassium salt heated in a Bunsen flame, there are produced, not thousands of images of the slit, representing as many different wave-lengths of light, but only two main images, one red, and one deep blue, corresponding to the two wave-lengths which are alone contained in high intensity in the original light. In a more powerful instrument other fainter lines are seen also. Naturally the brightness of all these lines is together equal to that of the original beam. No other substance

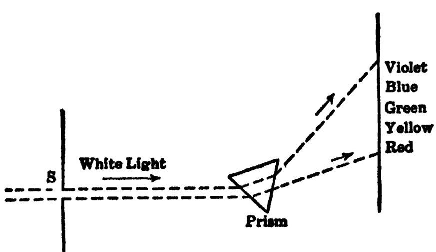


FIG. 192. Refraction of White Light by Prism.

gives any of those particular lines, although many others give blue and red light of somewhat different wave-lengths. Thus, strontium compounds give a blue light along with several red tints, but when strontium and potassium are used together, the lines are found not to be coincident. In the case of strontium, all the lines lie nearer to the yellow than in that of potassium. Since the whole light emitted is thus concentrated in one or two narrow strips, easily visible against a dark background, small amounts of the compounds give effects which are readily recognizable in the instrument. This remains true even when, to the eye, the colors are completely obscured by the much more brilliant, yellow light which compounds of sodium produce. In the spectrum of sodium, this yellow light is all concentrated into two yellow lines which lie very close together.

Helium gives many lines, but one orange line (D_3), in particular, was noted in the spectrum of the sun's photosphere many years before the element was obtained from terrestrial sources by Ramsay. When the spectra of helium and other gases are to be examined in the laboratory, a little of the material is enclosed in a narrow, exhausted tube, through which an electrical discharge can be passed between platinum wires. Under this treatment helium shows its conspicuous orange line, and hydrogen a red and two blue ones. In this apparatus compounds are dissociated and give the spectra of their constituents. When a Bunsen flame is used with the salts * of metals, however, the temperature is not high enough to render visible the spectra of the non-metals contained in them. Indeed, even of the metals themselves, only the members of the alkali and alkaline-earth groups give distinct results.

Rubidium and Caesium

Soon after the invention of the spectroscope by Bunsen and Kirchhoff, the instrument was applied to the examination of many substances. In 1860 Bunsen discovered several new lines in the spectrum given by materials derived from the salts in Dürkheim mineral water. Two new elements of the alkali group were found to cause their presence, and were named, from the colors of the lines which they gave, rubidium (red) and caesium (blue). Both elements have since been found in small quantities in various minerals. Rubidium is obtainable with relative ease from the mother-liquors of the Stassfurt works.

The metals may be obtained by heating their hydroxides with magnesium powder. The salts of these two elements are, in crystalline form and solubility, very much like those of potassium. In some cases the difference in solubility is sufficient to make separation possible. Thus, a mixture containing compounds of these two metals and of potassium gives with chloroplatinic acid a yellow precipitate, consisting of the three insoluble chloroplatinates. The solu-

* The chlorides are preferred because of their volatility. The salts of the oxygen acids are decomposed, and leave the highly involatile oxides.

bilities at 10°, however, are as follows: Potassium chloroplatinate 0.9, rubidium chloroplatinate 0.15, caesium chloroplatinate 0.05. Hence, when the mixed precipitates are carefully washed with small quantities of cold water the potassium chloroplatinate can be almost entirely removed. On similar principles the two other metals can be separated from one another. The iodides of all three elements combine with iodine, giving tri-iodides (compare p. 699), of which the tri-iodide of caesium is the most stable.

AMMONIUM

The compounds of ammonium claim a place with those of the alkali metals because in aqueous solution they give ammonium-ion NH_4^+, an ion which in its behavior closely resembles potassium-ion. Some of the special properties peculiar to ammonium compounds, and particularly the properties of ammonium hydroxide NH_4OH, have been discussed in detail already (pp. 513–15).

Salts of Ammonium. — **Ammonium chloride** NH_4Cl, known commercially as **sal ammoniac,** is prepared from the ammonia dissolved by the water used to wash illuminating gas (p. 625), or that obtained from by-product coke ovens. It is purified by sublimation, and then forms a compact fibrous mass. It crystallizes from solution in forms of the regular system, which are often arranged according to a feathery pattern. At 337.8° its vapor exercises one atmosphere pressure, and is dissociated into ammonia and hydrogen chloride to the extent of 62 per cent (see p. 514).

Ammonium nitrate NH_4NO_3 is a white crystalline salt which may be made by the interaction of ammonium hydroxide and nitric acid. When heated gently it decomposes, giving nitrous oxide and water (p. 537). It is used as an ingredient in fireworks and explosives.

Ammonium nitrate exists in no fewer than five distinct crystalline states under ordinary atmospheric pressure. The melted salt solidifies at about 170°, giving crystals of the regular system. When these are allowed to cool somewhat, and are held at a temperature a little below 125.5°, they change gradually into a mass of rhombohedral crystals, the density and all other physical properties altering at the same time. This temperature is a transition point like that at which monoclinic sulphur assumes the rhombic form (p. 544). When these rhombohedral crystals, in turn, are held at a temperature a little below 83°, they change their form once more into crystals which belong to the rhombic system and possess a third distinct set of physical properties. Below 35° a fourth change, into rhombic needles, takes place, and this state of

the substance is the one familiar at ordinary temperatures. Finally, at $-20°$, a fifth change in crystalline habit occurs! All these changes proceed in the reverse order when the temperature is elevated.

When ammonium hydroxide is treated with excess of carbon dioxide the solution gives, on evaporation, **ammonium bicarbonate** NH_4HCO_3. This is a white crystalline salt which is fairly stable at the ordinary temperature. It has, however, a faint odor of ammonia, and its dissociation becomes very rapid when slight heat is applied. When a solution of this salt is treated with ammonium hydroxide, the **normal carbonate** $(NH_4)_2CO_3$ is formed. But this salt, when left in an open vessel, loses ammonia very rapidly, and leaves the bicarbonate behind.

The substance commonly sold as ammonium carbonate is the so-called **sesquicarbonate**, and is made by sublimation from a mixture of ammonium chloride (or ammonium sulphate) and chalk or powdered limestone. It is a mixture, in approximately equi-molar proportions, of ammonium bicarbonate and **ammonium carbamate.** The latter is a substance related to **urea,** and formed when ammonia and carbon dioxide gases are mixed:

$$2NH_3 + CO_2 \rightarrow O{=}C\begin{matrix} \diagup NH_2 \\ \diagdown O-NH_4 \end{matrix}$$

Ammonium sulphate $(NH_4)_2SO_4$ is a white salt which is used chiefly as a fertilizer. By electrolysis of a concentrated solution of the **bisulphate** NH_4HSO_4, ammonium **persulphate** $(NH_4)_2S_2O_8$, which is less soluble, is formed and crystallizes out. It is used as an oxidizing agent (see p. 433).

Solutions of **ammonium-hydrogen sulphide** NH_4HS and **ammonium sulphide** $(NH_4)_2S$, made by passing hydrogen sulphide gas into ammonium hydroxide, are much used in analysis. The sulphide is almost completely hydrolyzed by water, giving the acid sulphide and ammonium hydroxide (compare sodium sulphide, pp. 406–9). It is used for the precipitation of sulphides, such as zinc sulphide ZnS, which are not sufficiently insoluble in water to be precipitated completely by hydrogen sulphide (see p. 411). Although even in ammonium sulphide solution the concentration of the $S^{=}$ ions is only minute, yet it is incomparably greater than in a solution of the exceedingly weak acid H_2S, and disturbance of the equilibrium by their removal, when they pass into combination, causes displacements which result in the generation of a continuous supply. The liquid smells strongly of ammonia and hydrogen sulphide on account of its hydrolysis. For the same reason, the salt is preferred to potassium or sodium sulphide in analysis,

since excess of the reagent can be driven out by simply boiling the mixture for a few minutes, all of the solution equilibria being reversed. Another application in analysis depends on the tendency of this salt to unite with certain insoluble sulphides, particularly those of tin, arsenic, and antimony (p. 684), giving soluble complex salts.

The solutions, when pure, are colorless. They dissolve free sulphur, giving yellow **polysulphides** (p. 411). The same yellow substances are also obtained by gradual oxidation of ammonium sulphide, when the solution of this salt is allowed to stand in a bottle from which the air is imperfectly excluded.

Ammonium Amalgam. — When a salt of ammonium is decomposed by electrolysis the NH_4^+, upon its discharge, ordinarily gives ammonia and hydrogen, and no free NH_4 is obtained. If, however, a pool of mercury is used as the negative electrode, the NH_4 forms an amalgam with it, and there seems to be reason to believe that this substance is actually present in solution in the mercury. While the amalgam is being formed it swells up and gives off the decomposition products above mentioned, so that the existence of free NH_4 is only temporary. The same material may be obtained by putting sodium amalgam into a concentrated solution of a salt of ammonium. The action is a displacement of one ion by another (p. 313):

$$Na \text{ (dissolved in Hg)} + NH_4^+ \rightarrow NH_4 \text{ (dissolved in Hg)} + Na^+.$$

This behavior is interesting since it is in harmony with the idea that ammonium, if it could be isolated, would have the properties of a metal. Substances other than metals are not miscible with mercury.

Ammonium-Ion NH_4^+: Analytical Reactions. — Ionic ammonium is a colorless substance. It unites with negative ions, giving salts, which, in the majority of cases, are soluble. Ammonium chloroplatinate $(NH_4)_2PtCl_6$, and to a less extent ammonium-hydrogen tartrate $NH_4HC_4H_4O_6$, are insoluble compounds, and their precipitation is used as a **test.** The surest means of recognizing ammonium compounds, however, consists in adding a soluble base to the substance (see p. 515). The ammonium hydroxide, which is thus formed, gives off ammonia on warming, and the latter may be detected by its odor.

Sodium Na

Occurrence. — Sodium chloride forms more than two-thirds of the solid matter dissolved in sea-water, and the great salt deposits are largely composed of it. Sea-plants contain mainly sodium salts of organic acids, just as land-plants contain potassium salts. **Chile saltpeter, cryolite,** and **albite** (a soda feldspar) **are important minerals.**

Preparation. — Sodium was first made by Davy (1807) by electrolysis of moist sodium hydroxide. It is now manufactured by the electrolysis of fused sodium hydroxide by a method invented by Castner. The cathode *C* projects through the bottom of the iron vessel containing the fused hydroxide (Fig. 193), and is held in place by a cake *S* of solid sodium hydroxide in the lower part of the vessel. This electrode is surrounded by a wire-gauze partition to permit circulation of the fused mass, but prevent escape of the globules of sodium. It is surmounted by a bell-shaped vessel of iron *B*, which floats in the fused alkali. In this the sodium and the hydrogen liberated at the cathode during the electrolysis collect. The atmosphere of hydrogen protects the fused metal from oxidation. The anode *A* is an iron cylinder surrounding the gauze and the oxygen collecting above it is allowed to escape through the vent *D*. The melted sodium is ladled out, from time to time, into molds, like candle molds.

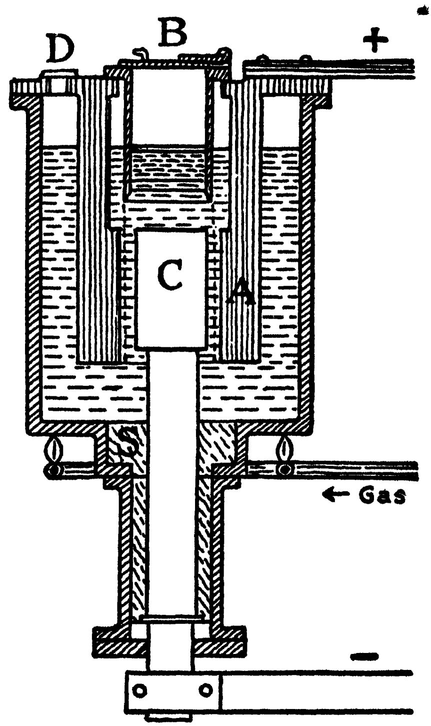


FIG. 193. Castner Process for the Manufacture of Sodium.

Methods have recently been developed for the production of sodium by large-scale electrolysis of fused sodium chloride. Dry chlorine is a valuable by-product.

Properties. — Sodium is a soft, shining metal, melting at 97.5° and boiling at 880°. The green vapor is chiefly monatomic (compare p. 698). The general chemical properties have already been given (p. 696). The metal unites with hydrogen to form a **hydride** NaH. Sodium is used in the manufacture of sodium peroxide and of many carbon compounds which are used as drugs and dyes. By contact action, it converts isoprene, an unsaturated hydrocarbon with the formula C_5H_8, into caoutchouc $(C_{10}H_{16})_n$ or raw rubber (see p. 651). Similar products

are obtained from the homologues (p. 577) of isoprene, the best results of all being given by methyl-isoprene, or dimethylbutadiene. This is a method of making rubber artificially. It cannot yet be carried out so cheaply as to compete with the natural product under ordinary circumstances, but in Germany during the war, when the supply of natural rubber was cut off entirely, considerable quantities of "methyl rubber" were manufactured from dimethylbutadiene by this synthetic method.

Sodium Chloride NaCl. — Common salt is obtained from the extensive salt deposits in various parts of the world. Since the salt can seldom be used directly, on account of impurities which it contains, it is purified by recrystallization from water. A certain amount is made, by evaporation, from sea water. The purest salt for chemical purposes it precipitated from a saturated solution of salt by leading into it hydrogen chloride gas (see p. 757).

Common salt crystallizes in cubes, which melt at 804°. It is the source of all sodium compounds, with the exception of the nitrate (see Fig. 194). From it come also most of the chlorine and hydrogen chloride used in commerce (see pp. 224, 238). It is a necessary article of diet, furnishing, for example, the hydrochloric acid in the gastric juice (p. 230).

The internal structure of a crystal of rock-salt, or sodium chloride, is given in Fig. 37, p. 68. The ions of sodium and of chlorine are arranged in two interpenetrating face-centered cubic lattices, and in such a way that every point of a simple cubic lattice is occupied. Each ion has *six* neighbors of opposite sign. This same structure, it may be mentioned, is exhibited by all of the halogen compounds of the alkali metals, with the exception of rubidium fluoride and the cæsium halides. Ammonium iodide has this form at ordinary temperatures, and ammonium chloride and bromide change over to it when the temperature is raised.

The halides of cæsium, and the modifications of ammonium chloride and bromide which are stable at ordinary temperatures, possess a different structure, the cube-centered cubic lattice (see Fig. 36). Here the ions of one sign are at the corners of a simple cubic lattice, and the ions of opposite sign are at the centers of these cubes. Each ion is thus surrounded by *eight* ions of opposite sign.

The Hydroxide and Oxides. — **Sodium hydroxide** NaOH, called also, colloquially, **caustic soda,** is prepared by the action of slaked lime upon sodium carbonate, but mainly by the electrolysis of a solution of sodium chloride (p. 233). Its general chemical properties and uses have already been discussed (Chapter XIII).

Sodium peroxide Na_2O_2 is made by heating sodium at 300–400° in air which has been freed from carbon dioxide. The sodium is

placed on trays of aluminium, and is passed into the furnace against the current of air. In this way, the freshest sodium meets the air from which most of the oxygen has been removed, and the action

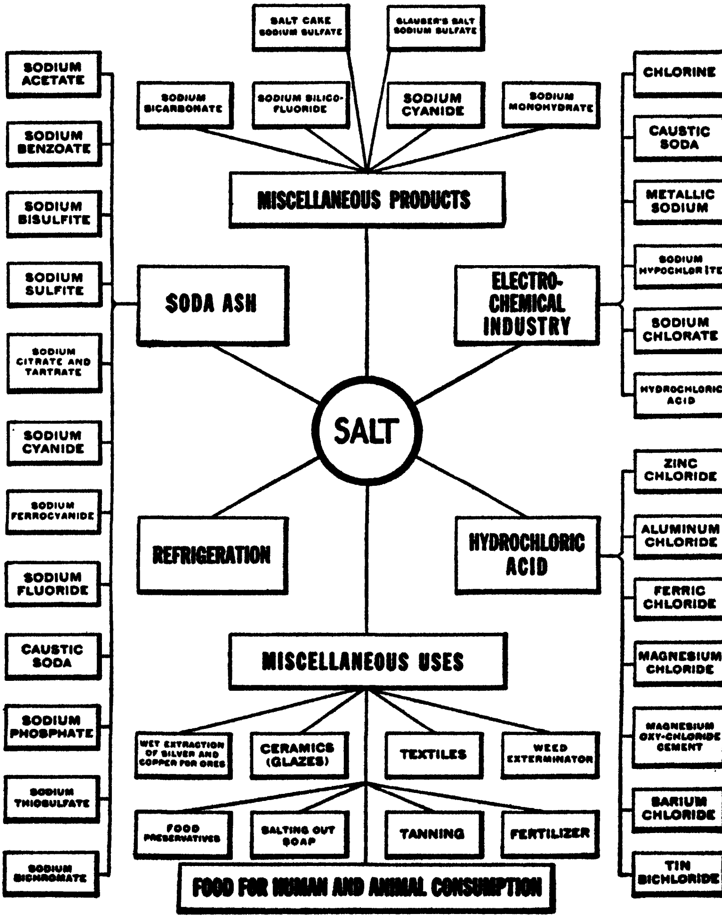


FIG. 194. The Industrial Position of Salt.

is moderated. Conversely, the almost entirely oxidized sodium meets the freshest air, and completion of the oxidation is thus assured.

This oxide is the sodium salt of hydrogen peroxide. When thrown into water it decomposes in part, in consequence of the heat devel-

oped, giving sodium hydroxide and oxygen. With careful cooling, however, much of it can be dissolved unchanged. By interaction with acids it yields hydrogen peroxide (p. 367). Sodium peroxide is now used commercially for oxidizing and bleaching and, in the form of oxone (p. 93), as a source of oxygen. The ordinary **sodium oxide** Na_2O is made in the same way as is potassium oxide (p. 701).

The Nitrate. — The occurrence of **sodium nitrate** $NaNO_3$ and its use in the manufacture of nitric acid have already been described (p. 521). Its crystals are rhombohedral. This salt is one of the best of fertilizers (see p. 612). It is used also in the manufacture of potassium nitrate (p. 702), and of sodium nitrite.

Sodium nitrite $NaNO_2$ is formed by heating sodium nitrate with metallic lead and recrystallizing the product (p. 535). Although very soluble it is less so than potassium nitrite, and is therefore more easily prepared in pure condition. It is used as a source of nitrous acid by manufacturers of organic dyes.

Manufacture of Sodium Carbonate. — Natural sodium carbonate is found in Egypt and in other parts of the world. At Owen's Lake, California, it is secured by solar evaporation of the water. The sesquicarbonate $Na_2CO_3,NaHCO_3,2H_2O$, being the least soluble of the carbonates of sodium, is the one deposited. Locally, small quantities of sodium carbonate are still made by the burning of seaweed. Up to the close of the eighteenth century this was the only source of the compound, and the product from Spain, known commercially as *barilla*, was ten times as expensive as the carbonate now is. Hence glass and soap were proportionately dearer than at present.

In 1791 the French Academy offered a prize for the discovery of an inexpensive method for the preparation of sodium carbonate from common salt, and **Le Blanc** proposed the process which bears his name and is still in use to a limited extent in Europe. During the Revolution his factory was destroyed, his patents were declared to be public property, and the inventor died by suicide. The chief stages of Le Blanc's process involve three chemical actions:

$$NaCl + H_2SO_4 \rightarrow Na_2SO_4 + 2HCl\uparrow$$
$$Na_2SO_4 + 2C \rightarrow Na_2S + 2CO_2\uparrow$$
$$Na_2S + CaCO_3 \rightarrow Na_2CO_3 + CaS.$$

Sodium chloride is treated at a red heat with an equivalent amount

of sulphuric acid, giving sodium *sulphate* Na_2SO_4. This "salt cake" is roasted with powdered coal and limestone. The coal reduces the sulphate to sodium *sulphide* Na_2S, and the latter interacts with the limestone giving sodium *carbonate* and calcium sulphide CaS. From this "black ash" the carbonate is separated by solution in water. The solution, when concentrated, gives crystals of the decahydrate, **washing soda** $Na_2CO_3,10H_2O$ (see p. 176). The latter, when heated, leaves "soda ash" or "calcined soda" Na_2CO_3.

The commercial survival of the Le Blanc process depends upon the economical recovery of the sulphur from the spent black ash (p. 399), and of the hydrogen chloride.

The **Solvay, or ammonia-soda process** (1860), has now displaced the Le Blanc process almost entirely. It differs from the latter by involving almost nothing but ionic actions. A solution of salt, saturated with ammonia and warmed to 40°, fills a tower divided by a number of perforated partitions. Carbon dioxide, made by heating limestone in special kilns, is forced in at the bottom. The perforations split up the gas into small bubbles, and facilitate its solution to form carbonic acid H_2CO_3. With the ammonium hydroxide NH_4OH in the liquid this gives ammonium bicarbonate:

$$NH_4OH + H_2CO_3 \rightleftarrows NH_4HCO_3 + H_2O.$$

The ammonium bicarbonate now interacts by double decomposition with the sodium chloride, and sodium bicarbonate, which is a much less soluble salt, is precipitated:

$$NaCl + NH_4HCO_3 \leftrightarrows NaHCO_3 \downarrow + NH_4Cl.$$

The solid sodium bicarbonate, after being freed from the liquid by filter-presses, is heated strongly and leaves behind sodium carbonate:

$$2NaHCO_3 \rightarrow Na_2CO_3 + H_2O \uparrow + CO_2 \uparrow.$$

The carbon dioxide which is liberated passes through the operation once more. The mother-liquor from the sodium bicarbonate contains ammonium chloride. This is decomposed by heating with quicklime from the kilns, and the ammonia which is thus obtained is available for the treatment of another batch.

A great deal of the sodium bicarbonate obtained by this process is used directly as **baking soda.**

Properties of the Carbonate and Bicarbonate. — The **decahydrate** $Na_2CO_3,10H_2O$ has a fairly high aqueous tension, and normally loses nine of the ten molecules of water which it contains when exposed in an open vessel (p. 176), leaving the monohydrate. At higher temperatures, or in a very dry atmosphere (p. 690), this in turn can be completely dehydrated. In aqueous solution, sodium carbonate is appreciably hydrolyzed (2.3 per cent in 0.1 *N* solution at 25°), and shows a marked alkaline reaction (p. 567). The compound is used in large amounts for the manufacture of glass and soap, and in the softening of water, and is applied in innumerable ways in the scientific industries for purposes akin to cleansing (see Fig. 195).

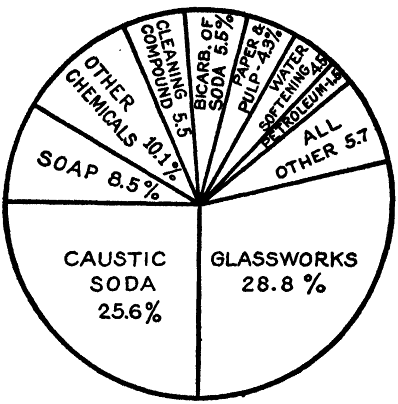


FIG. 195. Distribution of Soda Ash in Industry.

Sodium bicarbonate $NaHCO_3$ can be prepared in a state of purity by passing carbon dioxide over the decahydrate of sodium carbonate:

$$Na_2CO_3,10H_2O + CO_2 \rightleftarrows 2NaHCO_3 + 9H_2O.$$

This action is reversible (compare p. 724), and sodium bicarbonate shows, even in the cold, an appreciable tension of carbon dioxide. The aqueous solution of the *pure* substance is faintly alkaline (compare p. 566). The salt is used in the manufacture of baking powder and in medicine.

Other Salts of Sodium. — **Anhydrous sodium sulphate** Na_2SO_4 (thenardite) is found in the salt layers. The same salt is contained in mineral waters, such as those of Karlsbad. It is used, as a substitute for sodium carbonate, in making inexpensive glass.

The **decahydrate** $Na_2SO_4,10H_2O$ **(Glauber's salt)** forms large monoclinic crystals which give up all their water of hydration when kept in an open vessel. For the solubilities of the hydrate and anhydrous substance, see Fig. 88 (p. 208). When the decahydrate is mixed with concentrated hydrochloric acid, it is dehydrated, and double decomposition in the solution results in a precipitation of

sodium chloride, the second action being, of course, incomplete (see p. 330). This is one of those actions which proceed spontaneously, and therefore involve a diminution in the store of available energy in the system, although, so far as *heat* is concerned, a marked absorption of this form of energy takes place (see p. 258). The combination is used, in fact, as a freezing mixture.

Sodium thiosulphate $Na_2S_2O_3,5H_2O$ is made by boiling a solution of sodium sulphite with sulphur (p. 431). A standard solution (p. 337) of the thiosulphate is used in determining quantities of free iodine: $2Na_2S_2O_3 + I_2 \rightarrow 2NaI + Na_2S_4O_6$ (see p. 432).

When heated, dry sodium thiosulphate decomposes, giving sodium sulphate, which is the most stable oxygen-sulphur compound of sodium (see p. 417), and sodium pentasulphide:

$$4Na_2S_2O_3 \rightarrow 3Na_2SO_4 + Na_2S_5.$$

From the latter, four unit-weights of sulphur can be driven by stronger heating. Sodium thiosulphate is used for fixing negatives in photography (see p. 810), and by bleachers as an antichlor (p. 375).

Common **sodium phosphate** is a dodecahydrate of the secondary orthophosphate, $Na_2HPO_4,12H_2O$. It is made by neutralization of phosphoric acid with sodium carbonate. Its properties have already been discussed (p. 553).

Sodium tetraborate $Na_2B_4O_7,10H_2O$ (**borax**) has also been discussed under boron (p. 668). It is used as an ingredient in glazes for porcelain, in soldering, for bead reactions, and for preserving food.

Sodium disilicate $Na_2Si_2O_5$ (see pp. 661–2) is used for fireproofing wood and other materials, and for preserving eggs. Sand which is moistened with it and pressed in molds, forms, after baking, a serviceable artificial stone.

Properties of Sodium-ion Na^+: Analytical Reactions. — Sodium-ion is a colorless ionic material which unites with all negative ions. Practically all the salts so formed are soluble in water. The only ones which can be precipitated from dilute solution are sodium fluosilicate Na_2SiF_6, made by the addition of fluosilicic acid to a concentrated solution of a sodium salt, and sodium-hydrogen pyroantimonate $Na_2H_2Sb_2O_7$, made by similar addition of the corresponding potassium salt. All compounds of sodium confer a yellow color on the Bunsen flame, but this test is so delicate that it is shown (momentarily, at least) by the traces of sodium contained in almost all substances.

LITHIUM Li

The compounds of lithium are made from **amblygonite, a** mixed phosphate and fluoride of aluminium and lithium. It occurs also in **lepidolite** (a lithia mica) and in other rare minerals. Traces of compounds of the element are found widely diffused in the soil, and are taken up by plants, particularly tobacco and beets, in the ashes of which the element may be detected spectroscopically.

The **metal** is liberated by electrolysis of the fused chloride, the manipulation being facilitated by the addition of some potassium chloride to lower the melting-point of the lithium salt. The melting-point and boiling-point of the free element are higher than those of any other alkali-metal, and the specific gravity (0.53) is lower than that of any other metal whatever. Lithium floats not only upon water, but also in the petroleum in which it is preserved.

The metal behaves towards water and oxygen like sodium (p. 696). It unites directly and vigorously with hydrogen (LiH), nitrogen (Li_3N), and oxygen (Li_2O), forming stable compounds. In the fused state the hydride is a conductor of electricity, positive lithium-ion Li^+ traveling to the cathode and **negative hydride-ion** H^- (see p. 450) going to the anode. The relative insolubility (Table) of the hydroxide LiOH, the carbonate Li_2CO_3, and the phosphate $Li_3PO_4,2H_2O$, is in sharp contrast to the easy solubility of the corresponding compounds of the other alkali-metals, and links lithium with magnesium. The compounds of lithium give a bright-red color to the Bunsen flame, and a bright-red and a somewhat less bright orange line are seen in the spectrum. The carbonate is used in medicine.

Exercises. — 1. The vapor density of sodium peroxide has not been determined. Why is the formula Na_2O_2 assigned to it?

2. Why is potassium peroxide K_2O_4 and not KO_2?

3. Why should a mixture of potassium chlorate and antimony trisulphide be explosive?

4. How should you set about making, (*a*) a borate of potassium, (*b*) potassium pyrophosphate, (*c*) ammonium nitrite, (*d*) ammonium chlorate, (*e*) ammonium iodide?

5. In the Solvay process why is the ammonia dissolved in the salt solution, and not separately in water? Make the equation for the action of heat on limestone.

6. What is the exact percentage of water in washing soda?

7. Write full ionic equations for the Solvay process (p. 715).

8. Why does a solution of ammonium sulphide $(NH_4)_2S$ smell of ammonia and hydrogen sulphide?

9. Calculate the percentage compositions of schoenite and of kainite (p. 705).

10. Why, if ammonium hydroxide is really a strong base (see p. 514), is ammonium bicarbonate so much more unstable than sodium bicarbonate? [Formulate the hydrolysis of each in detail.]

11. What weight of (*a*) baking soda, (*b*) washing soda will be obtainable from 1000 kg. of common salt by the Solvay process, assuming 90 per cent recovery in both cases?

12. 10 c.c. of a solution containing free iodine are titrated with a 0.1 *N* solution of sodium thiosulphate, the end point being reached when 15.31 c.c. of the thiosulphate have been added (p. 717). What weight of free iodine did the solution contain per liter?

13. Why is the cleaning of platinum wires, as usually effected by holding them in the Bunsen flame, assisted by periodical dipping into hydrochloric acid (p. 707, footnote)?

14. One equivalent or *less* of concentrated sulphuric acid interacts in the cold with sodium carbonate to give normal sodium sulphate, and with sodium chloride to give sodium-hydrogen sulphate (p. 225). Why this difference? Which of the two products would be obtained by the action of cold concentrated sulphuric acid on, (*a*) sodium sulphite, (*b*) sodium nitrate, (*c*) sodium nitrite?

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CHAPTER XLIII

THE ALKALINE EARTH METALS

The Chemical Relations of the Elements. — The familiar metals of this group, **calcium** (Ca, atomic number 20), **strontium** (Sr, at. no. 38), and **barium** (Ba, at. no. 56), constitute a typical chemical family, both in the qualitative resemblance to one another of the elements and of the corresponding compounds, and in the quantitative variation in the properties with increasing atomic weight. In the electromotive series of the metals (p. 313), the members of this group fall just below the alkali metals. The metals themselves displace hydrogen vigorously from cold water, giving hydroxides. The solutions of these hydroxides, although dilute, on account of a rather small solubility, are strongly alkaline in reaction.

In all their compounds, calcium, strontium, and barium are **bivalent,** in correspondence with their position in the periodic system (p. 446). The hydroxides are formed by union of the oxides with water, and are progressively less easy to decompose by heating, barium hydroxide being the hardest. The carbonates, when heated, yield the oxide of the metal and carbon dioxide, barium carbonate being the most difficult to decompose. The nitrates, when heated moderately, give the nitrites, but the latter are broken up by further heating and yield the oxide of the metal and nitrogen tetroxide. In these and other respects the compounds of the metals of the alkaline earths resemble those of the heavy metals and differ from those of the metals of the alkalies. Barium approaches the latter most nearly.

The table of solubilities (inside front cover) shows that the chlorides and nitrates of calcium, strontium, and barium are all soluble in water, the solubility diminishing in the order given. The sulphates and hydroxides cover a wide range from slight solubility to extreme insolubility. Of the sulphates, 2000, 110, and 2.3 parts respectively, dissolve in one million parts of water at 18°. In the case of the hydroxides the order of magnitude is reversed, and

the corresponding numbers are 200, 630, and 2200. The carbonates are almost as insoluble as is barium sulphate.

The element **radium**, which also belongs to the alkaline earth family, has already been discussed in Chapter XXVI.

Calcium Ca

Occurrence. — The fluoride, and the various forms of the carbonate, sulphate, and phosphate, which are found in nature, are described below. As silicate, calcium occurs, along with other metals, in many minerals and rocks. Compounds of the element are found also in plants, and in the bones and shells of animals.

Calcium. — The metal is made by electrolyzing molten calcium chloride, to which calcium fluoride is added to lower the melting-point, in a graphite crucible, which forms the anode. The cathode is a rod of iron, one end of which dips into the fused salt. The calcium, liberated at this point, adheres to the rod. The latter is slowly raised, in such a way that the calcium always remains in contact with the liquid. In this fashion a long "cabbage-stalk" of calcium is finally produced.

Calcium is a silver-white, crystalline metal (m.-p. 810°, sp. gr. 1.55) which is a little harder than lead, and can be cut, drawn, and rolled. It burns in the air, giving a mixture of the oxide and **nitride** Ca_3N_2 (compare p. 505).

A white crystalline **hydride** CaH_2 is formed by direct union with hydrogen. It is known in commerce as **hydrolyte.** It is an expensive, but portable source of hydrogen for filling war balloons:

$$CaH_2 + 2H_2O \rightarrow Ca(OH)_2 + 2H_2.$$

Calcium Chloride $CaCl_2$. — Calcium-ion is present in small amount in sea-water, and hence compounds containing calcium chloride, such as **tachydrite** $CaCl_2,MgCl_2,12H_2O$, are found in salt deposits. The salt, for which there is insufficient commercial application to cover the available supply (see, however, Fig. 196), is formed in large quantities as a by-product in several industrial operations. Thus, it arises in the liberation of ammonia from ammonium chloride by the action of lime, in the manufacture of potassium chlorate (p. 384), and in the Solvay soda process (p. 715). By concentrating and cooling its aqueous solution the **hexahydrate**

of the salt, $CaCl_2,6H_2O$, is obtained below 30° in large, deliquescent, six-sided prisms. On account of the great concentration of a saturated solution of this compound, the solid and solution do not reach a condition of equilibrium with ice (see p. 217) until the temperature has fallen below —50°. The Solvay process by-product, when mixed with ice, gives, therefore, a very efficient freezing mixture. On account of its deliquescent character, the dehydrated salt, in granular form, is sprinkled on roads to lay the dust.

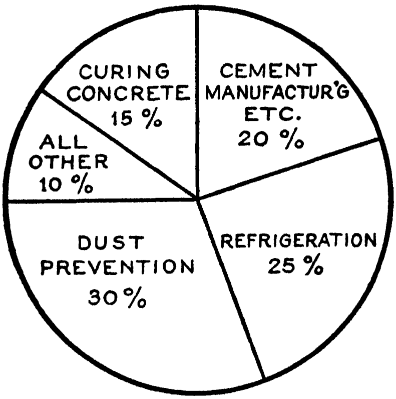


FIG. 196. Distribution of Calcium Chloride in Industry.

There are several other hydrates of calcium chloride containing less than $6H_2O$, and those containing less water exhibit lower aqueous tensions (compare p. 690), than have those containing more. By elevating the temperature, however, it is easy to raise the aqueous tension even of the monohydrate until it exceeds the partial pressure of water vapor in ordinary moist air, and so to drive out the water. To perform this rapidly, a temperature of over 200° is required. Partially dehydrated calcium chloride (approximately $CaCl_2,2H_2O$) forms a porous mass which is used in chemical laboratories for drying gases and liquids. Usually the dehydration is left incomplete, as, at the temperature required to complete it rapidly, some interaction with the water occurs: $CaCl_2 + H_2O \rightarrow CaO + 2HCl$, and a little free alkali is present in the product. When calcium chloride is used as a drying agent, it is naturally able to reduce the partial pressure of the water vapor only to the value of the aqueous tension of the hydrate system which is present, and no further. Even at low temperatures the aqueous tensions of hydrates are always perceptible. Concentrated sulphuric acid is a more thorough drying agent than is calcium chloride, and phosphorus pentoxide, the hydrated form of which (metaphosphoric acid) has no observable aqueous tension, is better still.

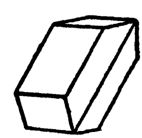
Calcium chloride forms molecular compounds, not only with water, but also with ammonia $CaCl_2,8NH_3$ and with alcohol. For drying these substances, therefore, quicklime is employed. Hydrogen sulphide interacts with the salt, giving hydrogen chloride, which

renders the gas impure. This gas is therefore dried with phosphorus pentoxide.

Calcium Fluoride CaF_2. — This compound occurs in nature as **fluorite** or **fluor-spar.** It crystallizes in cubes, is insoluble in water, and when pure is colorless. Natural specimens often possess a green tint or show a violet fluorescence. It is formed as a precipitate when a soluble fluoride is added to a solution of a salt of calcium.

Fluorite is used in the etching of glass, as the source of the hydrogen fluoride (p. 358). It is easily fusible, as its name indicates (Latin, *fluere,* to flow), and is employed in metallurgical operations as a flux (p. 683).

Calcium Carbonate $CaCO_3$. — The carbonate is the commonest compound of calcium. White **marble** is a pure variety, composed of crystals compactly wedged together. **Limestone** does not show much crystalline structure and usually contains clay and other impurities. **Chalk** is made up of shells of minute marine organisms. **Shells, coral,** and **pearls** are likewise mainly calcium carbonate. Well-formed crystals (**calcite,** or Iceland spar — Figs. 21 and 22, pp. 60–1 — and **aragonite** — Fig. 197) are common. Aragonite, when heated gently, resolves itself into a mass of minute crystals of calcite, and the latter is the more stable form of the substance. When calcium carbonate is produced by precipitation from cold solutions (*e.g.*, Na_2CO_3 and $CaCl_2$) the resulting crystals are calcite (at first so finely divided as to appear amorphous, but becoming coarser-grained and obviously crystalline on standing); while in warm solutions the less stable form, that of aragonite, is first assumed.


Fig. 197. Aragonite.

When heated, calcium carbonate dissociates, giving carbon dioxide and quicklime:

$$CaCO_3 \rightleftarrows CaO + CO_2 \uparrow .$$

At ordinary temperatures the decomposition is imperceptible. On the contrary, atmospheric carbon dioxide, in spite of its very low partial pressure, combines with quicklime, giving "air-slaked" lime. As the temperature rises, however, **the tension of carbon dioxide** coming from the carbonate increases, and **has a fixed value for each temperature.** If it is continuously allowed to escape, so that the maximum (equilibrium) pressure is not reached, the whole

of the salt eventually decomposes. At 700° this equilibrium pressure is only 25 mm., at 900° it reaches an atmosphere, and at 950° two atmospheres (see Fig. 198). If the carbon dioxide is *not* allowed to escape, the reaction ceases to progress as soon as the equilibrium pressure is attained. If *excess* pressure of CO_2 is induced, any CaO present will absorb CO_2 to reproduce $CaCO_3$. Only when the partial pressure of CO_2 is maintained constantly below the equilibrium pressure (as, for example, by driving a draft of air through the kiln) will the decomposition proceed to completion. The phenomenon is precisely similar to the evaporation of a pure liquid (p. 170) and to the dissociation of a hydrate (p. 176).

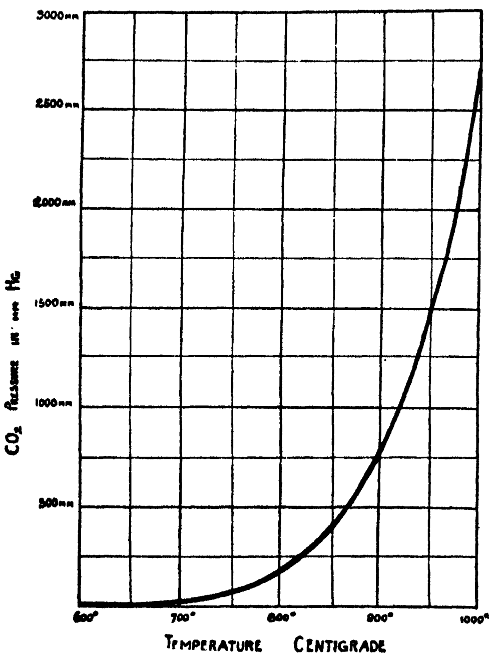


FIG. 198. Dissociation of Calcium Carbonate.

Limestone is soluble in water containing carbonic acid, giving calcium bicarbonate (p. 567). By solution of limestone, underground caves are often formed. Conversely, subterranean water containing the bicarbonate, when it reaches an open cavern, loses carbon dioxide and deposits limestone as **stalactites** or columns hanging from the ceiling. The drippings form **stalagmites** on the floors.

Limestone is used in the manufacture of quicklime and of glass. It is employed largely as a flux in metallurgy, when minerals rich in silica are brought into fusible form by the production of calcium silicate $CaSiO_3$. Large amounts also find application as building-stone.

The Phase Rule, a Method of Classifying all Systems in Equilibrium. — We can frequently abbreviate our statements by using two words of broad significance, one of which has already been employed. A set of materials in, or tending towards, a condition of equilibrium is called a **system**. The discrete

parts of an inhomogeneous system are called its **phases.** Thus, a liquid with its vapor forms a system with a liquid phase and a vapor phase. A saturated solution is a system with three phases, the undissolved excess of the solute (solid phase), the solution, and the vapor.

The formal resemblance that we have just shown to exist between the modes of behavior of a system composed of water and water-vapor in physical equilibrium, on the one hand, and of a system made up of calcium oxide, carbon dioxide, and undecomposed calcium carbonate in chemical equilibrium, on the other, is not a coincidence. A study of all kinds of systems in equilibrium shows that their different modes of behavior are limited in variety and can be classified in a very simple way.

The categories used for classification are: (1) the **independent components** in the system, and their number; (2) the distinct, physically separable parts or **phases** of the system, and their number; and (3) the **conditions** — temperature, pressure, and concentration — and the number of such conditions which may vary independently without the occurrence of a change in the number of the phases.

The mode of employment of these three categories may be illustrated in the order of their mention:

1. In the water and water-vapor system, water is the *only component.* In the calcium carbonate system, the independent components are *two* in number, calcium oxide and carbon dioxide.

2. In the water and water-vapor system there are *two phases,* the liquid phase and the vapor phase. In the calcium carbonate system there are *three phases* — two solid phases, the carbonate and oxide, and one gaseous phase, the carbon dioxide.

3. In the water and water-vapor system *either* the temperature *or* the pressure may be altered, within certain limits, at will. But, whichever one of these two conditions it be that is thus changed, *the preservation of the two phases* will at once require a simultaneous modification in the other condition, of such a nature as will suit the new value of the first. Thus, if the pressure upon the vapor is raised, the vapor phase will be destroyed unless the temperature is simultaneously elevated to a certain definite point (p. 167). Similarly, if the temperature is raised, the liquid phase will pass into vapor unless a sufficient increase in the pressure is simultaneously effected. There is therefore one, and only one **degree of freedom** in the conditions — the system is **univariant.** The experimenter has only *one* free choice, and after he has made this choice, the other condition necessary to preserve the number of phases is determined by the system. By a study of the calcium carbonate system, as described above, it will be seen that it also is a univariant system.

A partial generalization of these results leads to the conclusion that when the number of the phases exceeds the number of the components by *one,* the system is univariant. Additional illustrations are now required for reaching a still more general statement.

If ice be added to the water and water-vapor system, and the system be allowed to reach equilibrium with all three phases present, we find on analyzing as before: one component (water), three phases (solid, liquid, and gaseous), and no variability in the system. *Neither* temperature *nor* pressure may be altered without ensuing disappearance of one or other of the three phases. This system is therefore **invariant.** In the same way, if we consider a solution of potassium chloride in water, we note that an unsaturated solution

of given composition at a given temperature has a definite vapor pressure. As soon as we fix any two of the three variables (concentration, temperature, and pressure), the third is automatically fixed. The system consists of two components, two phases (solution and vapor) and is **bivariant.** However, if we take a *saturated* solution, with excess solid present, we find that at a given temperature it has a definite composition and a definite vapor pressure. Here we have two components, three phases, and only one degree of freedom. And finally, if we cool the saturated solution to a point where, as well as the salt, ice separates out as a solid phase, we have a system with four phases which is invariant.

It thus appears that with an equal number of components, the more phases we have, the more restricted are the possibilities of change in the conditions. When the number of phases equals the number of components, the system is bivariant; when the number of phases exceeds the number of components by one, the system is univariant; when the number of phases exceeds the number of components by two, the system is invariant, and, in general,

$$\textbf{Phases} + \textbf{Degrees of freedom} = \textbf{Components} + \textbf{2}.$$

The law, of which this equation is the most compact expression, is known as the **phase rule,** and was first formulated by Willard Gibbs, of Yale University. It applies to physical and chemical equilibria without distinction, and involves no consideration of molecules or atoms.

Thus, the formal resemblance between the dissociation phenomena exhibited by calcium carbonate and other compounds, on the one hand, and the behavior of a liquid in contact with its vapor on the other, is due simply to the fact that in each case the number of phases exceeds the number of components by one. This will be found to hold **in all cases** where there is, at each temperature, a constant dissociation pressure. A decomposing hydrate, for example, furnishes such a case. The system is made up of one gaseous phase (water vapor) and two solid phases (the hydrate, and the anhydrous substance or a lower hydrate). It has three phases and two components (water and the anhydrous substance), and is, therefore, univariant.

Again, when we have a sharp transition-point at a fixed temperature, that is, a unique temperature at which several different states of aggregation of a substance can co-exist (Fig. 79, p. 164), the system is always invariant. Thus, ice and water and vapor co-exist at the melting-point of ice (Fig. 93, p. 216): three phases and one component. Again, at 96° two solid forms of sulphur (p. 400) co-exist with sulphur vapor. In these cases the change which takes place at the transition point is purely *physical.* Analogous cases in which the change is a *chemical* one are equally familiar. The decahydrate of sodium sulphate decomposes (Fig. 88, p. 208) above 32.4°. At this temperature the decahydrate and the anhydrous salt co-exist with the saturated solution and water vapor: four phases and two components. The system is, therefore, invariant.

Some difficulty arises in certain systems, it must be noted, regarding the exact meaning of the term "independent component." The difficulty cannot be discussed in detail, for space considerations, and the student is recommended to refer to a special text such as Findlay's "The Phase Rule and Its Applications" (Longmans, Green and Co.). It will suffice to mention here that so long as the correct *number* of independent components is arrived at in the analysis of a complex system, a certain latitude in selecting from among the

substances present in the various phases to make up that number is frequently possible.

Calcium Oxide and Hydroxide. — Pure **oxide of calcium** CaO (**quicklime**) may be made by ignition of pure marble or calcite. For commercial purposes limestone is converted into quicklime in kilns (Fig. 199). The flames and heated gases from the fire pass between the pieces of limestone, and the carbon dioxide liberated is carried off by the draft. When the gas is to be used in the Solvay process or in the refining of sugar, coke (smokeless), instead of coal, is employed as the fuel. As low a temperature as possible is used. A high temperature causes impurities in the limestone (*e.g.*, clay) to interact with the quicklime, giving fusible silicates, which fill the pores and interfere with the subsequent slaking with water. Since the change is reversible, if the gas lingers in the kiln (at 760 mm. pressure), a temperature over 900° is required to drive the action forward (p. 724). However, a good draft, which removes the gas as fast as it is formed, permits the use of a lower temperature.

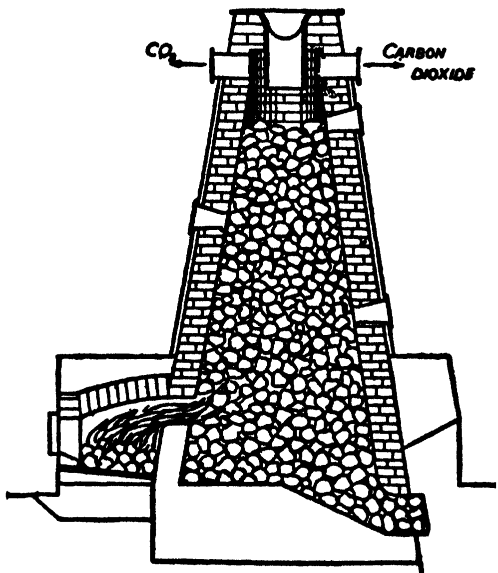


FIG. 199. Lime Kiln.

Pure calcium oxide is a white, porous solid. It is barely fusible in the oxyhydrogen flame (p. 139), but may be melted and vaporized in the electric arc.

When water is poured upon quicklime, it forms **calcium hydroxide** $Ca(OH)_2$. Much heat is evolved, and part of the water is turned into steam. The change is reversible, and at a high temperature the hydroxide (**slaked lime**) can be dehydrated. Quicklime from pure limestone slakes easily, and is known as "fat" lime. That made from material containing clay or magnesium carbonate is

"poor" lime. The latter slakes slowly and often incompletely, and, when used for mortar, does not harden so satisfactorily.

Calcium hydroxide is slightly soluble in water (**lime-water**), and the solubility decreases with rising temperature (see p. 205). On account of its cheapness, this substance is used by manufacturers in almost all operations requiring a base, and it thus occupies the same position amongst bases that sulphuric acid does amongst acids. When the presence of much water is unnecessary or undesirable, a suspension of the solid hydroxide in the saturated solution ("milk of lime"), or even a paste, is employed. Caustic lime is employed in the manufacture of alkalies, bleaching powder (p. 374), and mortar (see below), the purification of sugar (p. 603), the removal of the hair from hides in preparation for tanning, the softening of water (see p. 730) and as a whitewash.

Mortar. — Mortar is made by mixing slaked lime with three or four times its bulk of sand, and making the whole into a paste with water. When the water evaporates, a porous, rather crumbly material remains. This, however, at once begins to harden, owing to the action of the carbon dioxide in the air upon the lime:

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O \uparrow .$$

The crystalline calcite ($CaCO_3$) adheres to, and is interlaced with, the sand, and gives a rigid, though porous, structure attached firmly to the brick or stone. The pores facilitate the penetration of the air into the deeper parts and thus provide, both for the fresh supplies of carbon dioxide required for the continuance of the action shown in the equation, and for a considerable amount of useful ventilation through walls of the building.

Calcium Sulphate $CaSO_4$. — Calcium sulphate is a very common mineral. It occurs, as **anhydrite** $CaSO_4$, in salt deposits. **Gypsum** $CaSO_4,2H_2O$ is found in masses, and also in single crystals (**selenite,** Fig. 25, p. 61). **Alabaster** is highly crystalline gypsum, tinted by impurities.

Gypsum $CaSO_4,2H_2O$ is the commonest form, and is the one produced when calcium sulphate is precipitated. It is white and much softer than calcite. It is only slightly soluble in water (1 : 500 at 18°). It is used as a fertilizer and in making plaster of Paris and is the chief component of blackboard crayon or "chalk."

When gypsum is heated, the vapor pressure of the water it gives off soon exceeds that of the moisture in the atmosphere, and the compound begins to decompose:

$$2[CaSO_4,2H_2O] \rightleftarrows (CaSO_4)_2,H_2O + 3H_2O \uparrow .$$

The hemi-hydrate which remains (**plaster of Paris**) gives a much lower pressure of water vapor and is more stable. Plaster of Paris is manufactured in large quantities by heating gypsum in kilns. When moistened with water, it sets in about half an hour to a solid mass of gypsum. The temperature used in making it must not exceed 125°, otherwise the hemi-hydrate is itself decomposed, the plaster is "dead burnt," and it no longer sets readily. The setting involves, simply, the reversal of the equation given above.

Plaster of Paris swells somewhat, in setting, and so fills out completely every detail of a mold and applies itself closely to the outline of an object on which it is spread. It is used in making casts, and in surgical bandages where movable parts are to be held rigidly in place. **Stucco** is made with sizing or glue instead of pure water.

What Makes Water Hard. — All natural waters except rain water, which is "soft," contain salts of calcium and magnesium in solution and are more or less "hard." These salts are dissolved by the water in its passage over and through the soil.

Although limestone is very insoluble in pure water (0.013 g. per liter), yet it interacts with the carbonic acid contained in all natural waters, giving **calcium bicarbonate,** which is about thirty times more soluble under atmospheric conditions:

$$CO_2 + H_2O \rightleftarrows H_2CO_3 + CaCO_3 \rightleftarrows Ca(HCO_3)_2.$$

When the water is boiled, these actions are all reversed. The carbon dioxide is driven out of solution, the carbonic acid is decomposed, and the calcium bicarbonate gives calcium carbonate, most of which is at once precipitated. Iron carbonate is also held in solution as bicarbonate $Fe(HCO_3)_2$ and is precipitated as $FeCO_3$ by boiling. These two bicarbonates constitute **temporary hardness.** Their decomposition causes the "fur" in a kettle.

The sulphates of calcium (solubility 2 g. per liter) and of magnesium (very soluble) are also commonly found in natural waters. These salts are not altered by boiling, but remain in solution and give **permanent hardness** to the water.

Consequences of Hardness in Water. — When hard water is used in a steam boiler, the salts, of course, are not carried off with the steam, but accumulate amazingly as fresh water is injected and steam alone is drawn off. In time, heavy deposits of *boiler crust* settle on the tubes of the boiler, and interfere with the transference of heat from the metal to the water. One-fourth of an inch of crust will increase the bill for fuel by 50 per cent. In addition to this the iron is heated to a higher temperature and may even become red hot. In consequence, it combines more rapidly with oxygen on the outside and displaces hydrogen from the water (p. 130) on the inside, giving in both cases Fe_3O_4. Thus the life of the boiler is shortened. If the formation of the crust is not prevented, or if the crust is not removed, the boiler may explode and great damage may be done.

When hard water is used for *washing*, in the *household* or *laundry*, much soap has to be dissolved before the necessary lather can be secured. Soap, which consists of a mixture of the sodium salts of several organic acids, such as palmitic acid $H.CO_2C_{15}H_{31}$ (see p. 639), interacts by double decomposition with the salts of calcium and magnesium giving palmitates, etc., of these metals. These salts are insoluble and form a "curd." With sodium palmitate $Na(CO_2C_{15}H_{31})$, for example, the action is:

$$CaSO_4 + 2Na(CO_2C_{15}H_{31}) \rightarrow Ca(CO_2C_{15}H_{31})_2 \downarrow + Na_2SO_4.$$

Not until all the salts causing the hardness have been decomposed does the permanent solution of soap which is required for washing begin to be formed. The waste thus involved is often very great and expensive.

Treatment of Hard Water. — *Temporary* hardness is commonly removed, on a large scale, by adding *slaked lime* in *exactly the quantity* shown by an analysis of the water to be required, and stirring for a considerable time:

$$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2CaCO_3 \downarrow + 2H_2O. \qquad (1)$$

The bicarbonate is neutralized and the carbonate which is precipitated is removed by filtration.

Permanent hardness is not affected by slaked lime, but is removed by adding sodium carbonate in the necessary proportion:

$$CaSO_4 + Na_2CO_3 \rightarrow CaCO_3 \downarrow + Na_2SO_4. \qquad (2)$$

When *both kinds of hardness are present,* crude caustic soda (sodium hydroxide) may be employed. It neutralizes the bicarbonate, precipitating $CaCO_3$:

$$Ca(HCO_3)_2 + 2NaOH \rightarrow CaCO_3 \downarrow + Na_2CO_3 + 2H_2O \qquad (3)$$

and giving sodium carbonate. The latter then acts as in equation (2).

In the **permutite process** (Fig. 200) the water is simply filtered through an artificial sodium silico-aluminate (permutite) which is

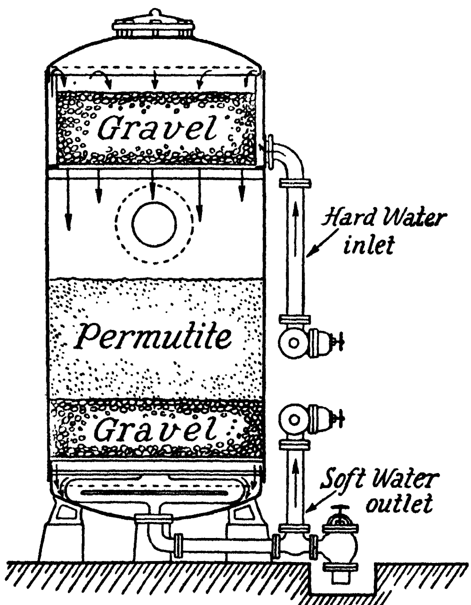


FIG. 200. Permutite Process for Water Softening.

supplied in the form of a coarse sand. The calcium, etc., in the water is exchanged for sodium, which does no harm. If we use for permutite the abbreviated formula $Na\overline{P}$, we may write the reaction thus:

$$Ca(HCO_3)_2 + 2Na\overline{P} \rightarrow 2NaHCO_3 + Ca\overline{P}_2.$$

After twelve hours' use, the permutite is covered with 10 per cent

salt solution and allowed to remain for the other twelve hours of the day, when it is ready for employment once more:

$$2NaCl + Ca\overline{P}_2 \rightarrow CaCl_2 + 2Na\overline{P}.$$

Only salt, which is inexpensive, is consumed, and calcium chloride solution is thrown away. Permutite removes magnesium, iron, manganese, and other elements in the same way. The life of a charge is said to be over twenty years.

Hard Water in the Laundry. — As we have seen (p. 730), soap *will* soften water, but the calcium and magnesium salts of the soap acids, which are precipitated, are sticky, and soil the goods being washed. Other substances that soften water not only give non-adhesive precipitates, but are also much cheaper, and an attempt is generally made to utilize them. The use of slaked lime on a small scale is impracticable.

Washing soda $Na_2CO_3,10H_2O$ is added to precipitate both kinds of hardness:

$$Ca(HCO_3)_2 + Na_2CO_3 \rightarrow CaCO_3\downarrow + 2NaHCO_3$$
$$CaSO_4 + Na_2CO_3 \rightarrow CaCO_3\downarrow + Na_2SO_4.$$

The small amounts of salts of sodium which remain in the water have no action on soap.

Household ammonia NH_4OH acts like sodium hydroxide (p. 731):

$$Ca(HCO_3)_2 + 2NH_4OH \rightarrow CaCO_3\downarrow + (NH_4)_2CO_3 + 2H_2O$$
$$CaSO_4 + (NH_4)_2CO_3 \rightarrow CaCO_3\downarrow + (NH_4)_2SO_4$$

except that it will *not* precipitate magnesium-ion.

When *borax* $Na_2B_4O_7,10H_2O$ (p. 668) is added, it is hydrolyzed and the sodium hydroxide contained in its solution acts as already described.

The supposed bleaching or whitening action of borax or soda is a myth; these salts *prevent staining by the iron* in the water. They simply precipitate the iron (present as $Fe(HCO_3)_2$), which almost all waters contain, as $FeCO_3$ *before* the goods are put in. This precipitate is easily washed out in rinsing. The palmitate, etc., of iron, however, which the soap itself would throw down, is sticky and adheres to the cloth. The air subsequently oxidizes it and gives hydrated ferric oxide (rust), which is brownish-red.

It is evident that, properly to achieve their purpose, the soda and borax

must be added, must be completely dissolved, and must be allowed to produce the precipitation of $FeCO_3$, $CaCO_3$, etc., all *before* the soap, or the goods, is introduced. If the soap is dissolved before or with the soda, *it* will take part in the precipitation, and give sticky particles containing the iron and calcium salts of the soap acids.

Other Salts of Calcium. — **Bleaching-powder** (p. 374), calcium **nitrate** (p. 531), calcium **bisulphite** (p. 417), and the **phosphates** of calcium (p. 613) are elsewhere discussed. Calcium **sulphide** in solution is used as a depilatory, since the proteins contained in hair and wool are decomposed by, and dissolved in alkaline solutions, like that here formed by its hydrolysis.

Ordinary calcium sulphide, after it has been exposed to sunlight, usually shines in the dark. Barium sulphide behaves in the same way. On this account these substances are used in making **luminous paint.** They apparently owe this behavior to the presence of traces of compounds of vanadium and bismuth, for the purified substances are not affected in the same fashion.

The use of calcium **silicate** $CaSiO_3$ in glass manufacture has already been described.

Calcium **oxalate** CaC_2O_4 may be observed under the microscope in the cells of many plants. Since it is the least soluble common salt of calcium, its formation by precipitation is used as a **test** for calcium ions.

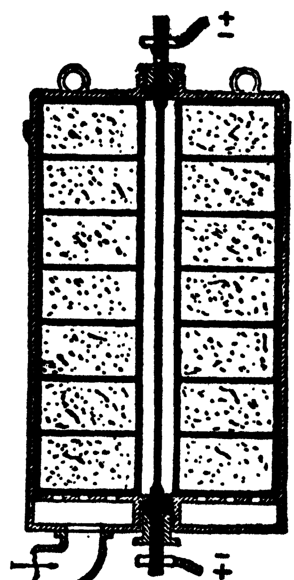


FIG. 201. Manufacture of Nitro-Lime.

The manufacture of calcium **carbide** CaC_2 in the electric furnace has been taken up in an earlier chapter (p. 563).

The structural formula of calcium carbide is of interest, inasmuch as it not only illustrates the chemical behavior of the substance but also explains the apparently anomalous valences of its constituent elements. Calcium carbide CaC_2 is evidently related in constitution to acetylene C_2H_2, since it evolves this gas on treatment with water. Acetylene has the formula $H-C\equiv C-H$, and calcium carbide is consequently $Ca\begin{matrix}\diagup C\\ \quad |||\\ \diagdown C\end{matrix}$, one bivalent calcium atom substituting for two hydrogen atoms.

In a sense, it is permissible to regard acetylene as an extremely weak acid, and calcium carbide as a salt of this acid, readily hydrolyzed by water. Similarly methane, although it exhibits none of the usual properties of an acid (see p. 581), gives easily-hydrolyzed salts like aluminium carbide Al_4C_3. Even the *nitrides*, such as Mg_3N_2, may be considered as salts derived from the exceedingly weak acid N_3H, just as the *oxides* are salts derived from the exceedingly weak acid H_2O (p. 318).

Calcium Cyanamide $CaCN_2$. — Calcium carbide, when strongly heated, absorbs nitrogen, giving a mixture of calcium cyanamide and carbon (**nitro-lime**):

$$CaC_2 + N_2 \rightarrow CaCN_2 + C.$$

The carbide is pulverized and placed in a cylindrical furnace (Fig. 201), holding 300 to 450 kg. The heat (800° to 1000°) is furnished by the passage of a current of electricity through a thin carbon rod, which passes through the axis. The tube surrounding the rod and the other partitions are of cardboard, which burns up and leaves openings for the circulation of the nitrogen. The latter is made by the fractionation of liquid air and is introduced under pressure. In thirty-five hours nitrogen ceases to be absorbed, and the sintered product is pulverized when cold.

Calcium cyanamide is now manufactured in large quantities at Niagara Falls (Ontario) and Odda (Norway) for use as a **fertilizer.** It is also a valuable source of ammonia, and was utilized very extensively as such for the manufacture of **explosives** during the Great War. When treated with hot water, calcium cyanamide is decomposed as follows:

$$CaCN_2 + 3H_2O \rightarrow CaCO_3 + 2NH_3.$$

In practice, pulverized nitro-lime is fed into an autoclave charged with water. Impurities such as free calcium carbide and calcium phosphide are immediately decomposed, and the gases evolved allowed to escape. Small amounts of alkali are then added to facilitate the evolution of ammonia and to prevent the formation of complex nitrogen compounds. The autoclave is closed and steam admitted until the pressure rises to 3–4 atmospheres, the heat evolved by the decomposition of the cyanamide being sufficient to carry the reaction to rapid completion. The ammonia given off is absorbed in water, or converted directly to ammonium sulphate. When the gas ceases to be given off, steam is blown through the

liquor in the autoclave until all residual dissolved ammonia is expelled.

Nitro-lime, when fused with sodium carbonate, gives **sodium cyanide** NaCN, used in the extraction of gold (p. 812):

$$CaCN_2 + C + Na_2CO_3 \rightarrow CaCO_3 + 2NaCN.$$

Calcium-Ion Ca^{++}: Analytical Reactions. — Ionic calcium is colorless. It is bivalent, and combines with negative ions. Many of the resulting salts are more or less insoluble in water. Upon the insolubility of the carbonate, phosphate, and oxalate are based tests for calcium-ion in qualitative analysis (see p. 738). The presence of the element is most easily recognized by the brick-red color its compounds confer on the Bunsen flame, and by two bands — a red and a green one — which are shown by the spectroscope.

STRONTIUM Sr

The compounds of strontium resemble closely those of calcium, both in physical properties and in chemical behavior.

Occurrence. — The carbonate of strontium $SrCO_3$ is found as **strontianite** (Strontian, a village in Argyllshire), and is isomorphous with aragonite. The sulphate, **celestite** $SrSO_4$, is more plentiful. It shows rhombic crystals which are isomorphous with those of anhydrite, often have a blue color, and are commonly associated with native sulphur in specimens from Sicily. The metal may be isolated by electrolysis of the molten chloride.

Compounds of Strontium. — The common salts (chloride, nitrate, etc.) are all made from the natural carbonate or sulphate. The former may be dissolved directly in acids, and the latter is first reduced by means of carbon to the sulphide, and then treated with acids.

Strontium-ion Sr^{++} is bivalent, and gives insoluble compounds with carbonate-ion, sulphate-ion, and oxalate-ion. The presence of strontium is recognized by the carmine-red color which its compounds give to the Bunsen flame (see also p. 738). Its spectrum shows several red bands and a very characteristic blue line. Salts of strontium, such as the nitrate, are used in the manufacture of red lights for fireworks and signals.

Barium Ba

The physical and chemical properties of the compounds of barium also recall those of calcium.

Occurrence. — Like strontium, barium is found in the form of the carbonate, **witherite** $BaCO_3$, which is rhombic and isomorphous with aragonite, and the sulphate $BaSO_4$, **heavy-spar** or **barite** (Greek βαρύς, heavy), which is rhombic and isomorphous with anhydrite. The density of the sulphate is 4.5, while that of other compounds of the light metals does not generally exceed 2.5. The free metal, which is silver-white, may be obtained by electrolysis of the molten chloride.

The compounds are made by treating the natural carbonate with acids directly, or by first reducing the sulphate with carbon to sulphide, or converting the carbonate into oxide, and then treating the products with acids.

Compounds of Barium. — Natural **barium sulphate** $BaSO_4$ is the source of many of the compounds. The precipitated sulphate, made by adding sulphuric acid to the aqueous extract from barium sulphide, is used in making white paint ("blanc fixe"), in filling paper for glazed cards, and sometimes as an adulterant of white lead (p. 833). A mixture of barium sulphate and zinc sulphide ZnS, prepared in a special way, is called **lithopone:**

$$BaS + ZnSO_4 \rightarrow BaSO_4 \downarrow + ZnS \downarrow .$$

Made into paint it has greater covering power than white lead, does not darken with hydrogen sulphide as does the latter, and is non-poisonous. Barium sulphate is highly insoluble in water and is hardly at all affected by aqueous solutions of any chemical agents. It is somewhat soluble in pure (100%) sulphuric acid, and the solution yields crystals of a molecular compound $BaSO_4,H_2SO_4$. Calcium and strontium sulphates behave in the same way. All three compounds are decomposed by addition of sufficient water, and give the insoluble sulphates.

Barium monoxide BaO is manufactured from the carbonate. This, however, demands a much higher temperature than does calcium carbonate for its decomposition, the equilibrium tension of carbon dioxide not reaching one atmosphere until above 1350°,

Special means must therefore be exployed to assist the reaction. Heating with powdered charcoal is very efficient:

$$BaCO_3 + C \rightarrow BaO + 2CO.$$

The oxide unites vigorously with water to form the hydroxide.

The monoxide, when heated in a stream of air or oxygen, gives **barium peroxide**: $2BaO + O_2 \rightleftarrows 2BaO_2$, as a compact gray mass. This change and its reversal constituted the basis of **Brin's process** for obtaining oxygen from the air (p. 90). To protect the oxide from conversion into the carbonate and hydrate, which are not decomposable at the temperature employed, the air must be carefully purified from carbon dioxide and moisture (compare p. 712).

A hydrated form of barium peroxide is thrown down as a crystalline precipitate when hydrogen peroxide solution is added to a solution of barium hydroxide:

$$Ba(OH)_2 + H_2O_2 \leftrightarrows BaO_2 \downarrow + 2H_2O.$$

The crystals have the formula $BaO_2,8H_2O$. Similar hydrates of the peroxides of strontium and calcium may be made in the same way, In all three cases the pure peroxides are obtained as white powders by removal of the water of hydration by very gentle heating *in vacuo* (compare p. 690). The peroxides of strontium and calcium are not formed by direct union of oxygen with the oxides. Barium peroxide is used in the manufacture of hydrogen peroxide (p. 367).

Barium hydroxide $Ba(OH)_2$ is the most soluble of the hydroxides of this group, and gives, therefore, the highest concentration of hydroxyl-ion. The solution is known as "baryta-water." It is also the most stable of the three hydroxides, and may be melted without decomposition. A hydrate $Ba(OH)_2,8H_2O$ crystallizes on cooling a saturated solution. It is much used in quantitative analysis for making standard alkali-solutions. Solutions of sodium or potassium hydroxide may acquire varying proportions of carbonate by the action of carbon dioxide from the air, and their action on indicators loses thereby in sharpness. With barium hydroxide this is impossible, for the carbonate is insoluble, and is precipitated from the solution.

Barium-ion Ba^{++} is a colorless, bivalent ion. Many of its compounds are insoluble in water, and the sulphate is insoluble in dilute acids also. The spectrum given by the salts contains a number of green and orange lines. The Bunsen flame is colored green. Salts

of barium are employed, therefore, to give a green light in fireworks and night signals.

Distinction between Calcium, Strontium and Barium Compounds. — The flame tests, described above, offer the quickest method of recognition.

In solutions of salts of calcium, strontium, and barium, the ions may be distinguished by the fact that calcium sulphate solution will precipitate the strontium and barium as sulphates, but will leave salts of calcium in dilute solution unaffected. Similarly, strontium sulphate solution precipitates barium sulphate, and does not give any result with salts of the first two. The chromate of barium is precipitated in presence of acetic acid, while the chromates of strontium and calcium are not (compare p. 764), and there are other differences of a like nature in the solubilities of the salts.

A precipitate of $CaSO_4$ is readily soluble in concentrated HCl, while a precipitate of $BaSO_4$ is not. The explanation of this difference (for a more detailed and general discussion, see next chapter) is to be found by studying the effect of addition of H^+ upon the solubility equilibria of $CaSO_4$:

$$CaSO_4 \text{ (solid)} \rightleftarrows Ca^{++} + SO_4^{=}.$$

Obviously, if we can decrease either $[Ca^{++}]$ or $[SO_4^{=}]$ in the saturated solution, more $CaSO_4$ must dissolve (p. 272). Now the addition of H^+ in high concentration involves the reaction (p. 428):

$$H^+ + SO_4^{=} \rightleftarrows HSO_4^-.$$

and so reduces $[SO_4^{=}]$ very materially. If we look closely into the mechanism of the reaction in which $CaCO_3$ is brought into solution by the action of CO_2 (p. 729), we find that its essential feature is an analogous process:

$$H^+ + CO_3^{=} \rightleftarrows HCO_3^-.$$

When then, does $BaSO_4$ not dissolve, in the same way, when we add HCl? Because $BaSO_4$ is so *extremely insoluble* that, however large a concentration of H^+ is added, its effect is quite insignificant. Barium sulphate *can* be brought into solution by means of 100 per cent sulphuric acid (p. 736), but the controlling factor here is the formation of the molecular compound $BaSO_4$, H_2SO_4.

Exercises. — 1. Arrange the chromates of the metals of this family in the order of solubility (see Table on inside front cover). Compare the solubilities with those of the carbonates, oxalates, and sulphates.

2. Why do lime-water and baryta-water become milky when kept in an open bottle?

3. What will be the ratio by volume, at 150°, of the nitrogen tetroxide and oxygen given off by the decomposition of calcium nitrate? What would be the nature of the difference between the ratio at 150° and that at room temperature (see p. 528)?

4. Construct a scheme of equilibria showing the hydrolysis of calcium sulphide in aqueous solution. Why does the presence of calcium hydroxide diminish the tendency to hydrolyze (p. 409)?

5. Why does whitewash become so firmly attached to the wall?

6. What is the percentage of nitrogen in nitro-lime, assuming 100 per cent efficiency of conversion?

7. Make equations for the action of sodium palmitate: (*a*) upon calcium bicarbonate; (*b*) upon magnesium sulphate.

8. In softening water: (*a*) what would be the objection to using an excess of slaked lime; (*b*) why is prolonged stirring required (p. 728); (*c*) why must the precipitate be removed by filtration?

9. Explain why wood ashes are sometimes used to soften water, and how they act.

10. Why does fluorite lower the melting-point of a slag?

11. To a saturated solution of calcium sulphate, ammonium oxalate is added. Formulate and explain the reaction that occurs, using the solubility data on the inside front cover.

12. What weight of hydrolyte (p. 721) will be required to fill a balloon, with a capacity of 10,000 cubic feet, with hydrogen at 20° and 800 mm.?

13. 100 g. of $CaCO_3$ are heated in a closed vessel, with a capacity of 100 liters, to 800°. Use Fig. 198 (p. 724) to calculate what percentage of the $CaCO_3$ will be decomposed when equilibrium is reached.

14. Would it make any difference in Exercise 13 if the vessel were full of air at the start, or if it were evacuated? Give a reason for your answer.

15. What weights of the following materials would be required to remove the hardness from 1000 cubic feet of water saturated with calcium sulphate (solubility 2.0 g. per liter) at 20°: (*a*) soap (sodium palmitate, p. 730); (*b*) washing soda (p. 732)?

16. What weight of ammonia will be obtained by the action of excess water and steam upon 1000 kg. of nitro-lime ($CaCN_2 + C$)?

17. How would you distinguish between the following precipitates: calcium carbonate, calcium phosphate, calcium sulphate, calcium oxalate, calcium hydroxide, calcium fluoride?

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CHAPTER XLIV

MAGNESIUM AND ZINC. IONIC EQUILIBRIA CONSIDERED QUANTITATIVELY

The remaining elements of the third column of the periodic table, namely **beryllium** (Be, atomic number 4), **magnesium** (Mg, at. no. 12), **zinc** (Zn, at. no. 30), **cadmium** (Cd, at. no. 48), and **mercury** (Hg, at. no. 80), although all **bivalent,** do not form a coherent family. Beryllium and magnesium resemble zinc and cadmium, and differ from the calcium family, in that the sulphates are soluble, the hydroxides easily lose water, and the metals are not rapidly rusted in the air and do not easily displace hydrogen from water. They resemble the calcium family, and differ from zinc and cadmium, in that the sulphides are hydrolyzed by water, the oxides are not reduced by heating with carbon, and the metals do not enter into complex ions (p. 687). But beryllium differs from magnesium and resembles zinc in that its hydroxide is acidic as well as basic. This is not unnatural, since in the periodic system it lies between lithium, a metal, and boron, a non-metal.

Mercury is the only member of the group that forms two series of compounds. These are derived from the oxides HgO and Hg_2O. Mercury approaches the noble metals in the ease with which its oxides are decomposed by heating, and in the position of the free element in the electromotive series. The other members of the present group are all well above hydrogen in this series (see p. 313), and displace hydrogen from dilute acids. In deference to its abnormalities, we shall postpone the discussion of mercury to a later chapter, where it will be taken up in conjunction with copper, an element which resembles it most closely in its chemical relations.

BERYLLIUM Be

Chemical Relations of the Element. — Beryllium is bivalent in all its compounds. Its oxide and hydroxide are basic, and are also feebly acidic towards active bases (see Zinc hydroxide). On account of this fact and the extreme ease with which its carbonate gives up carbon dioxide, in both of which respects it resembles alu-

minium (p. 768), it was first thought to be trivalent. This made its atomic weight 13.53, the amount combining with one chemical unit of chlorine being 4.51. In the periodic system, however, there was a space for a bivalent element with the atomic weight 9.02 ($= 2 \times 4.51$) between lithium and boron, and none for a trivalent element. Later (1884) Nilson and Pettersson determined the vapor density of the chloride and of certain organic compounds of the element, and found only 9.02 parts of beryllium in the molar weights of the compounds. The element was formerly called also *glucinum*, with the symbol Gl, from the sweet taste of its salts (Greek γλυκυς, sweet).

The Metal and its Compounds. — Beryllium occurs in beryl, a metasilicate of beryllium and aluminium $Al_2Be_3(SiO_3)_6$. Specimens of beryl tinted green by the presence of a little silicate of chromium are known as **emeralds.** The metal may be obtained by electrolysis of the easily fusible double fluoride $BeF_2,2KF$. In powdered form it burns when heated in the air. It displaces hydrogen from dilute acids, and also, when heated, from caustic potash: $Be + 2KOH \rightarrow K_2BeO_2 + H_2$. The oxide interacts with acids and with strong bases. The salts give no color to the Bunsen flame. Since beryllium is one of the lightest metals (sp. gr. 1.85), alloys containing it have been developed for use in aircraft construction, and the demand for such alloys is growing considerably.

Magnesium Mg

Chemical Relations of the Element. — Magnesium is bivalent in all its compounds. The oxide and hydroxide are basic exclusively. The element does not enter into complex cations or anions.

Occurrence. — Magnesium carbonate occurs alone as **magnesite,** and in a double salt with calcium carbonate $MgCO_3,CaCO_3$ as **dolomite.** The sulphate and chloride are found as hydrates and as constituents of double salts (pp. 614, 705) in the Stassfurt deposits. Silicates are also common. **Olivine** is the orthosilicate Mg_2SiO_4. **Serpentine** is a hydrated disilicate, $[Mg,Fe]_3Si_2O_7,2H_2O$ (see foot-note on p. 812), as is also meerschaum. **Asbestos** is an anhydrous silicate. **Talc** (soapstone) is $H_2Mg_3(SiO_3)_4$. The element derives its name from Magnesia, a town in Asia Minor.

Asbestos, a fibrous material, is used in making fireproof cloth and cardboard. Soapstone is made into sinks and table tops for use, for example, in laboratories.

The Metal. — Magnesium is now manufactured most readily by electrolysis of the oxide MgO dissolved in a bath of the molten fluoride (for details see Aluminium, p. 768). Another common method of obtaining the metal is by electrolyzing a molten mixture of magnesium, calcium, and sodium chlorides. A carbon rod forms the anode, and the iron crucible the cathode, on which the metal collects in globules. The mass, when cold, is broken up and the metal is recast in bars. The metal is silver-white, and when heated can be pressed into wire and rolled into ribbon (m.-p. 651°, b.-p. 1100°). Commercial specimens of the latter often contain zinc.

Chemically the metal is less active than are the metals of the alkaline earths. It slowly becomes coated with a layer of a basic carbonate, which is non-coherent and so does not protect the metal from rusting completely. It displaces hydrogen slowly from boiling water, and rapidly from cold, dilute acids. Magnesium burns in air with a white light, rich in rays of short wave-length such as act upon photographic plates (p. 811). The ash contains a *nitride* Mg_3N_2, as well as the oxide. The former interacts with water to give ammonia (p. 505). When the metal is heated with the oxides of boron, of silicon, and of many of the metals, it combines with the oxygen and liberates the other element.

The United States' production of magnesium in 1935 exceeded 20,000 tons. Until recently the main use of the element was as a deoxidizing agent in the manufacture of other metals (compare the use of aluminium by steelmakers, p. 770), but now parts fabricated from magnesium or its alloys are proving increasingly advantageous in reducing the dead weight of busses, trucks, trailers, aeroplanes, and portable equipment of all types. Magnesium filings, mixed with potassium chlorate, give **flash-light powder.** Signal lights are made of shellac, barium nitrate and magnesium powder.

Oxide MgO and Hydroxide $Mg(OH)_2$. — The **oxide** is made by heating magnesium carbonate, and is therefore called **calcined magnesia.** Being very infusible ("refractory") it is used in lining electric furnaces. On account of its poor heat conductance, it is also employed very extensively for insulating pipes and boilers, and so reducing heat losses (**85% Magnesia**). It combines slowly with water, giving the **hydroxide** $Mg(OH)_2$, which with water gives a paste that hardens under the action of the carbon dioxide of the air (see mortar, p. 728). The oxide is *basic,* and with acids gives salts by double decomposition.

Magnesium hydroxide $Mg(OH)_2$, being insoluble, is easily precipitated by adding sodium hydroxide to a solution of a salt of magnesium. When moistened and mixed with a little magnesium chloride, it sets to a hard basic chloride of variable composition. The mixture, to which sawdust is sometimes added, is used as a plaster in house decoration.

Magnesium hydroxide is **not** precipitated by addition of ammonium hydroxide to a solution of a magnesium salt *when salts of ammonium are also present in quantity in the solution.* Conversely, precipitated magnesium hydroxide interacts with solutions of ammonium salts and passes into solution. The reason for this will be developed later on in the chapter (pp. 751–64).

Salts of Magnesium. — **Magnesium carbonate** $MgCO_3$ is found in nature. Only hydrated *basic* carbonates are formed by precipitation, and their composition varies with the conditions. The carbonate manufactured in large amounts and sold as **magnesia alba** is approximately $Mg_4(OH)_2(CO_3)_3,3H_2O$. It is used in tooth powder and for polishing silver. The carbonates are not precipitated in the presence of ammonium salts, and interact with such salts in the same way as does the hydroxide (see above).

Magnesium sulphate $MgSO_4$ is commonly sold as the heptahydrate, $MgSO_4,7H_2O$, **Epsom salt.** It is found in the salt deposits and in many aperient mineral waters. Thus **Hunyadi water** contains little beside 47 g. Epsom salt and 52 g. sodium sulphate ($Na_2SO_4,10H_2O$) and 1 g. sodium bicarbonate per liter. The salt is used for loading cotton goods and as a purgative.

Magnesium chloride $MgCl_2$ is found in sea water and in some natural waters. It occurs in the Stassfurt deposits, alone, and as **carnallite** $MgCl_2,KCl,6H_2O$. The latter is a most important source of potassium chloride (p. 614), and almost all the magnesium chloride combined with it is thrown away. Magnesium chloride is very deliquescent (p. 213) and, being present in impure table salt, causes the latter to cake or even become moist in damp weather. Addition of a very little sodium bicarbonate to the salt remedies this difficulty. Magnesium chloride is a very objectionable form of hardness in water, because hot water partially hydrolyzes the salt and liberates hydrochloric acid, which attacks and corrodes the iron of the boiler and tubes. Hence sea water cannot be used in marine boilers.

The only important **phosphate** is **ammonium-magnesium orthophosphate** $NH_4MgPO_4,6H_2O$, which appears as a crystalline precipitate when sodium phosphate and ammonium hydroxide (and chlo-

ride, contrast magnesium hydroxide, p. 743) are mixed with a solution of a magnesium salt. This compound is insoluble in water containing ammonium hydroxide, and is used in quantitative analysis for estimating both magnesium and phosphoric acid. Before being weighed the precipitate is ignited, and is thus converted into the anhydrous pyrophosphate of magnesium $Mg_2P_2O_7$. The salt $NH_4MgAsO_4,6H_2O$ has similar properties, and is used for estimating arsenic acid.

Analytical Reactions of Magnesium Compounds. — The magnesium ion is colorless and bivalent. Soluble carbonates precipitate basic carbonates of magnesium, but not when ammonium salts are present. The latter limitation distinguishes compounds of magnesium from those of the calcium family. Sodium hydroxide precipitates the hydroxide of magnesium, except when salts of ammonium are present. The mixed phosphate of ammonium and magnesium, in presence of ammonium hydroxide, is the least soluble salt.

Zinc Zn

Chemical Relations of the Element. — Zinc is bivalent in all its compounds. Of these there are two sets, — the more numerous and important one, in which zinc is the positive radical ($ZnSO_4$, $ZnCl_2$, etc.), and a less numerous set, the zincates, in which zinc is included in the negative radical ($Na_2.ZnO_2$, etc.). Zinc is the first of the metals which we have, so far, studied in detail to exhibit compounds of this latter type. Many other metals, however, will be found to behave similarly in subsequent chapters (compare p. 771). Both sets of salts are hydrolyzed by water, as the hydroxide is feeble whether it is considered as an acid or as a base. The salts are all **poisonous.**

Occurrence and Manufacture. — Zinc is found in nature mainly as **zinc blende** ZnS (in large amounts in Missouri) and **smithsonite** $ZnCO_3$ (Spain and U.S.). Other ores of zinc are **calamine** Zn_2SiO_4,H_2O, **franklinite** $Zn(FeO_2)_2$, and **zincite** ZnO. The red color of the last is due to the presence of manganese.

In the case of the carbonate ore, the oxide ZnO is first obtained by heating. When zinc blende ZnS is the ore, it is crushed and pulverized, concentrated by flotation (see p. 785), and then roasted (p. 414) to remove the sulphur and leave the oxide:

$$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2.$$

The ore is fed in at the top of a huge, box-like furnace (Fig. 202, diagrammatic) through which rush the flames and heated gases from fuel gas burning with an excess of air. The ore is turned over and gradually displaced forward by moving rakes until, at the end, it drops to the next level. Here it is raked in the opposite direction, until it falls to the third level. The ore collects at the bottom fully oxidized, while the sulphur dioxide in the gases is made into sulphuric acid. The oxide from either ore is then reduced by heating with powdered coal:

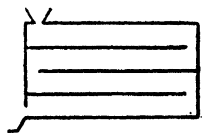


FIG. 202. Furnace for Roasting Zinc Ores.

$$ZnO + C \rightarrow Zn + CO.$$

This treatment of zinc ores should be carefully considered. Since ores of most metals consist of the carbonate, sulphide, or oxide of the metal, these steps are common to most metallurgical processes. In the case of other metals, only the forms of the furnaces and other details vary.

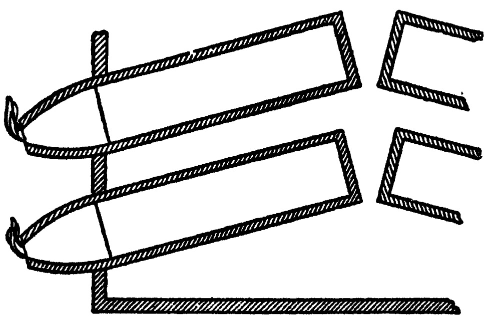


FIG. 203. Manufacture of Spelter.

In the case of zinc, because it is a *volatile* metal, the heating of the mixture of oxide and coal is conducted in *retorts,* from which the metal issues as *vapor.* The mixture is placed in fire-clay cylinders (4 to 5 ft. long), which are arranged in several tiers in an oblong, gas-heated furnace (Fig. 203). A fire-clay receiver is luted on with clay. The carbon monoxide burns with a blue flame at the nozzle of each receiver, while the zinc condenses to liquid within it. From time to time the liquid metal is raked out into a traveling iron pot, from which it is poured into molds. The metal, in this form, is called **spelter.** It contains small amounts of lead, arsenic, iron and cadmium.

Electrolytic methods (see Chapters XLVI and XLIX) of obtaining zinc have recently come into extensive use. The world's production of zinc in 1935 amounted to 1,311,000 metric tons (382,000 in the United States).

Properties and Uses of the Metal. — Zinc is a bluish-white, crystalline metal. When cold it is brittle, but at 120–150° it can be rolled into sheets between heated rollers and then retains its pliability when cold. At 200–300° the metal becomes once more brittle, at 419.4° it melts, and at 907° it boils. The vapor density at 1740° is 2.38 (air = 1), and the molecular weight, therefore, 2.38 × 28.955 (p. 185) or 68.9. The gas is thus monatomic.

The metal burns in air with a greenish flame, giving zinc oxide. When cold it is not affected by dry air, but in moist air it is oxidized, and becomes covered with a firmly adhering, non-porous layer of basic carbonate which protects it from further action. The metal displaces hydrogen from dilute acids, but with pure specimens the action almost ceases in consequence of the formation of a layer of condensed hydrogen on the surface. Contact with a less electropositive metal, such as lead, iron, copper, or platinum, enables the action to go on, because the hydrogen is then liberated at the surface of the other metal (see Electromotive chemistry). Crude zinc containing lead and iron is therefore more active than pure zinc. Zinc also attacks boiling alkalies, giving the soluble zincate (see p. 748): $2KOH + Zn \rightarrow K_2ZnO_2 + H_2$. The action on ammonium hydroxide is slower and different in nature:

$$Zn + 2H_2O + 4NH_3 \rightarrow Zn(NH_3)_4.(OH)_2 + H_2,$$

a complex cation being formed.

Sheet zinc, in consequence of its lightness (density 7), is used in preference to lead (density 11.5) for roofs, gutters, and cornices. Iron is coated (**galvanized**) with zinc by thorough cleaning with dilute sulphuric acid or the sand blast, and dipping in melted zinc. Iron netting, corrugated iron for sheds and roofing, and iron gutters, tanks, and pipes are coated with zinc, either in this way, or by electroplating (see p. 809). **Sherardized iron** is made by covering the article with zinc dust and baking it. The zinc protects the iron, primarily because it excludes the air from the surface, and secondarily because, even when the coating is broken, the zinc, being the more active metal of the two (p. 142) is rusted first. Zinc is used also in extracting silver from crude lead (p. 805), as the active metal in batteries (p. 847), and in several alloys (*e.g.*, Babbitt metal, p. 694, brass, and German silver). It mixes in all proportions with tin, copper, and antimony, but with molten lead and bismuth separation into two layers occurs, each metal dissolving only a little of the other. The two different modes of behavior

resemble those of alcohol and water and ether and water (p. 200), respectively.

In the laboratory **granulated zinc,** made by pouring the melted metal in a thin stream into water, and **zinc dust** (impure, contains ZnO), are the forms commonly employed.

Zinc Chloride $ZnCl_2$. — This salt is usually manufactured by treating zinc with *excess* of hydrochloric acid, evaporating the solution to dryness, and fusing the residue. When hydrochloric acid is thus present, the chloride $ZnCl_2$ is obtained as a white, deliquescent solid. Evaporation of the pure aqueous solution, which is acid in reaction, results in considerable hydrolysis and formation of much of the basic chloride Zn_2OCl_2:

$$ZnCl_2 + H_2O \rightleftarrows HCl + Zn(OH)Cl, \qquad (1)$$
$$2Zn(OH)Cl \rightarrow Zn_2OCl_2 + H_2O. \qquad (2)$$

The salt is **used** in solid form as a caustic. Its aqueous solution *gelatinizes cellulose* and *dissolves it* (p. 600), and thus is used in parchmentizing paper and in impregnating wood (*e.g.*, railway sleepers) to prevent decay. The aqueous solution, being acid by hydrolysis, is used for cleaning the surface of metals before **soldering.** Solder (see p. 829) "runs" on a hot brass, copper, or lead surface, *provided the latter is clean,* and adheres perfectly when cold. But it does not dissolve oxides, or melt them, and therefore cannot even reach the surface of the metal, much less adhere to it, if the slightest tarnish is present.

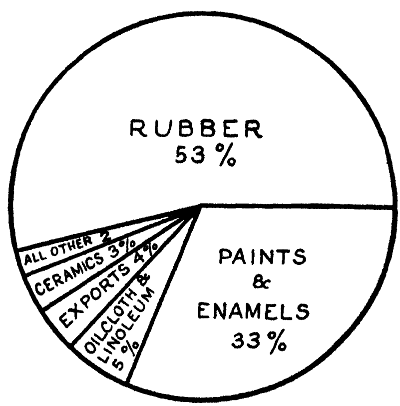


FIG. 204. Distribution of Zinc Oxide in Industry.

Zinc Oxide and Hydroxide and the Zincates. — The oxide ZnO is obtained as a white powder by burning zinc or by heating the precipitated basic carbonate. It turns yellow when heated, recovering its whiteness when cold in the same way that mercuric oxide is brown whilst hot and bright red when cold. It is

used (Fig. 204) in making a paint — zinc-white or Chinese white — which is not darkened by hydrogen sulphide. It is also used as a filler in rubber automobile tires. For filling teeth, dentists sometimes use a paste made by mixing the oxide with a concentrated solution of zinc chloride. It quickly sets to a hard mass of oxychloride.

The **hydroxide** $Zn(OH)_2$ of zinc appears as a white, flocculent solid when alkalies are added to solutions of zinc salts. It interacts as a basic hydroxide with acids, giving salts of zinc:

$$Zn(OH)_2 + H_2SO_4 \rightleftarrows ZnSO_4 + 2H_2O.$$

It also interacts with excess of the alkali employed to precipitate it, giving a soluble **zincate,** such as **potassium zincate** K_2ZnO_2:

$$H_2ZnO_2 + 2KOH \rightleftarrows K_2ZnO_2 + 2H_2O.$$

Both actions are reversible, and the second requires a considerable excess of alkali for its completion: in fact, some of the zinc hydroxide seems to be simply in colloidal suspension. It is evident that zinc hydroxide when in solution is ionized **both as an acid and as a base:**

$$\begin{array}{c} 2H^+ + ZnO_2^= \rightleftarrows Zn(OH)_2 \text{ (dissolved) } \rightleftarrows Zn^{++} + 2OH^- \\ \upharpoonleft\downharpoonright \\ Zn(OH_2) \text{ (solid).} \end{array}$$

Substances which are both bases and acids are called **amphoteric.** The ionization of zinc hydroxide as an acid is less than that as a base, but both are small. Addition of an acid like sulphuric acid, however, furnishes hydrogen-ion; the hydroxyl ions combine with this to form water, and all the equilibria are displaced to the right. With a base, on the other hand, hydrogen-ion is removed and the basic ionization simultaneously repressed, so that the equilibria are displaced to the left.

Zinc hydroxide interacts with ammonium hydroxide, giving the soluble **ammonio-zinc hydroxide** $Zn(NH_3)_4.(OH)_2$. In a solution of this substance, the zinc is existent almost entirely as part of a complex positive ion $[Zn(NH_3)_4]^{++}$. Consideration of this point will be deferred until Chapter XLVII, when it will be taken up in detail in connection with similar complex ions of copper.

Other Compounds. — Zinc sulphate, $ZnSO_4$, is formed by oxidation when zinc-blende is roasted. It gives, on recrystallization from water, rhombic crystals of the hydrate $ZnSO_4,7H_2O$. This, and

the corresponding compounds of magnesium $MgSO_4,7H_2O$, of iron $FeSO_4,7H_2O$, and of several other bivalent metals, are all isomorphous, and are known as **vitriols.** The zinc salt is **white vitriol.** It is **used** in preserving hides, as a mordant in cotton-printing (see dyeing, p. 640), and as an eye-wash (1/8 per cent solution).

Zinc sulphide ZnS (white) is precipitated practically completely when a solution of ammonium sulphide $(NH_4)_2S$ is added to a salt of zinc:

$$ZnSO_4 + (NH_4)_2S \rightarrow ZnS \downarrow + (NH_4)_2SO_4.$$

When hydrogen sulphide is employed instead:

$$ZnSO_4 + H_2S \rightleftarrows ZnS + H_2SO_4$$

only a small part of the zinc is precipitated. The cause of this difference will come up for discussion in a subsequent section (p. 760). For the use of zinc sulphide as a paint ingredient (**lithopone**), see p. 736.

The **normal zinc carbonate** $ZnCO_3$ may be precipitated by means of sodium bicarbonate:

$$ZnSO_4 + 2NaHCO_3 \rightarrow Na_2SO_4 + ZnCO_3 + H_2O + CO_2.$$

The normal carbonate of sodium, however, gives **basic carbonates,** such as $Zn_2(OH)_2CO_3$, which, as in the case of magnesium (p. 743), vary in composition according to the conditions.

Analytical Reactions of Zinc Salts. — Zinc sulphide is precipitated by the addition of ammonium sulphide to solutions of zinc salts and of zincates. Sodium hydroxide gives the insoluble hydroxide, which, however, interacts with excess of the alkali, giving the soluble zincate of sodium. Compounds of zinc, when heated on charcoal with cobalt nitrate, give a zincate of cobalt, Rinmann's green $CoZnO_2$.

Cadmium Cd

Chemical Relations of the Element. — This element is bivalent in all its compounds. Its oxide and hydroxide are basic exclusively, and the salts are not hydrolyzed by water. It enters into complex compounds having the ions $Cd(NH_3)_4^{++}$, $Cd(CN)_4^{=}$, and $CdI_4^{=}$.

The Metal. — Aside from the rare mineral **greenockite** CdS, cadmium is found only in small amounts (about 0.5 per cent), as carbonate and sulphide, in the corresponding ores of zinc. During the reduction, being more volatile than zinc, it distils over first (b.-p. 767°). The metal is white, and is much more malleable than is zinc. It melts at 321°.

It displaces hydrogen from dilute acids, but is itself displaced from solutions of its compounds by zinc, since it is less electropositive.

Cadmium was formerly the unwanted step-child of zinc, its only use being in making fusible alloys. Recently, however, a large demand has sprung up from the automobile industry for cadmium-plated nuts, bolts, and other small parts, and for cadmium-nickel and cadmium-silver alloys as bearing metals. Cadmium-red pigments are also coming into extensive use.

Compounds of Cadmium. — The **chloride** $CdCl_2,2H_2O$ is efflorescent and is not hydrolyzed during dehydration or in solution (contrast with zinc, p. 747). The halides are less ionized than are the corresponding compounds of most other metals. The iodide CdI_2, in particular, seems to exist in solution as $Cd.CdI_4$, and the complex anion gives little ionic cadmium. On account of this fact even the sulphide cannot be precipitated completely from a solution of the iodide. Conversely, hydriodic acid dissolves the sulphide to a much greater extent than do other acids.

The white **hydroxide** is made by precipitation, and interacts as a basic hydroxide with acids, but is not amphoteric, and consequently does not react at all with active bases. It dissolves in ammonium hydroxide, however, forming $Cd(NH_3)_4.(OH)_2$. The **oxide** CdO is a brown powder, obtained by heating the hydroxide, carbonate, or nitrate, or by burning the metal.

The **sulphate** crystallizes as $3CdSO_4,8H_2O$, and is not isomorphous with the sulphates of zinc and magnesium. Soluble carbonates throw down the **normal carbonate** $CdCO_3$, and not a basic carbonate.

Hydrogen sulphide precipitates the yellow **sulphide** CdS even from acid solutions of the salts. The substance is used as a pigment. The sulphide of cadmium, however, is less insoluble in water than are the sulphides of copper and mercury, and therefore cannot be precipitated from a strongly acid solution (*e.g.*, HCl > 0.3 *N*).

The Solubilities of the Sulphides of the Metals. — The reader will remember the order of solubility of the metallic sulphides more easily if he notes

that it is practically the same as the order of activity of the free metals (p. 142). Thus, the sulphides down to that of aluminium are dissolved by water (K_2S and Na_2S), or are decomposed by water (BaS, SrS, CaS, MgS, Al_2S_3). The hydroxides formed being fairly soluble (except $Al(OH)_3$), a clear solution is obtained except in the case of Al_2S_3. Ferrous sulphide is insoluble in water, but is soluble enough to interact with (and dissolve in) dilute acids to some extent, even with a feeble one like acetic acid. Zinc sulphide requires a dilute *active* acid; cadmium sulphide requires a higher concentration of an active acid, as do also CoS and NiS; cupric sulphide requires an oxidizing acid like hot nitric acid; and mercuric sulphide resists even this.

Analytical Reactions of Cadmium Compounds. — The cadmium ion Cd^{++} is bivalent and colorless. The yellow cadmium sulphide is precipitated by hydrogen sulphide, even from acid solutions of the salts. It is also precipitated from solutions containing the complex cation $Cd(NH_3)_4^{++}$ and the complex anion $Cd(CN)_4^{=}$, as, for example, from a solution made by adding excess of potassium cyanide to cadmium chloride solution ($K_2.Cd(CN)_4$). The latter property enables cadmium to be separated from copper (p. 793). The white hydroxide is thrown down by sodium hydroxide, and is not soluble in excess of this reagent. It is not formed from solutions containing the $Cd(NH_3)_4^{++}$ and $Cd(CN)_4^{=}$ ions, and interacts with ammonium hydroxide to give the soluble $Cd(NH_3)_4(OH)_2$. The above precipitations are not complete when cadmium iodide $Cd.CdI_4$ is used.

Ionic Equilibria Considered Quantitatively

In view of the predominance of ionic actions in the chemistry of the metals, and of the determinative effect of ionic equilibria on many actions, it is essential that we should be prepared in future for a more exact study of these phenomena than we have hitherto attempted. The whole *basis* for this exact study *has already been supplied* and only more specific application of the principles is demanded. The basis referred to, which should now be read, is contained in the discussion of chemical equilibrium in general (pp. 272–4) and of ionic equilibrium (pp. 326–7) in particular.

In the case of the dissociation of phosphorus pentachloride:

$$PCl_5 \rightleftarrows PCl_3 + Cl_2$$

we saw that the point of equilibrium at any given temperature was dependent upon the molecular concentration of each reactant, and that the extent of the dissociation could therefore be changed not

only by change of pressure but also by addition of an excess of either of the dissociation products, PCl_3 or Cl_2. However much the point of equilibrium might be varied, nevertheless, the **equilibrium constant** $[PCl_3].[Cl_2]/[PCl_5]$ remained unchanged. In the case of the ionization of acetic acid, similarly:

$$CH_3COOH \rightleftarrows H^+ + CH_3.COO^-,$$

we found that while the degree of dissociation increased as the concentration was decreased, yet the **ionization constant** $[H^+].[CH_3.COO^-]/[CH_3.COOH]$ did not vary. It remains now to discuss in detail, in this latter case, the effect upon the point of equilibrium of addition of excess of either of the dissociation products, H^+ or $CH_3.COO^-$, and to examine how far the results obtained are applicable to other types of electrolytes.

Excess of One Ion. — In the case of hydrogen sulphide (p. 410), we showed that increasing the concentration of the hydrogen-ion displaced the equilibrium by favoring the union of the ions to form molecular hydrogen sulphide: $2H^+ + S^= \rightleftarrows H_2S$. This we speak of **as a repression of the ionization** of the hydrogen sulphide. Now, if the electrolyte is already only *slightly* ionized, like a weak acid or a weak base, the repression of the ionization through the formation of molecules in this way may remove so many of that one of the ions which is not present in excess (corresponding to the $S^=$ in the foregoing illustration), that the mixture will no longer respond to tests for the ion so removed. This is an interesting and very common case.

Thus, as we have seen on p. 316, a normal solution (60 g. in 1 liter) of acetic acid is only 0.004 ionized, so that, in the equation for the equilibrium,

$$(0.996)\ CH_3.COOH \leftrightarrows H^+\ (0.004) + CH_3.COO^-\ (0.004),$$

the relative proportions are as shown by the numbers in parentheses. If the whole of the acid (60 g.) were ionized, there would be 1 g. of hydrogen-ion per liter. Yet, even in the much smaller concentration actually present (0.004 g. per liter), the acid taste of the H^+ and its effect upon indicators can be distinctly recognized. If, now, solid *ammonium acetate* (which is quite neutral with respect to indicators) is dissolved in the solution, the liquid *no longer gives an acid reaction* with one of the less delicate indicators, like methyl orange (see p. 339). The explanation is simple. Ammonium ace-

tate, as a typical salt, is practically completely ionized. It gives, therefore, a large concentration of acetate-ion to a liquid formerly containing very little. This causes a greatly increased union of the H^+ ions and CH_3COO^- ions to occur, and the former, being already very few in number, disappear almost entirely. Hence the solution becomes, to all intents and purposes, neutral. There is no less *acetic acid* present than before, but the concentration of hydrogen-ion is very much smaller.

Formulation and Quantitative Treatment of the Case of Excess of One Ion. — If $[H^+]$ and $[CH_3.COO^-]$ represent the *molecular concentrations* of hydrogen-ion and acetate-ion, respectively, and $[CH_3.COOH]$ that of the acetic acid molecules at equilibrium, then:

$$\frac{[H^+] \cdot [CH_3.COO^-]}{[CH_3.COOH]} = K.$$

The value of this *ionization constant* K will not change, whether the concentration of the solution of acetic acid is great or small, and even when another substance with a common ion is present. In the latter case, $[CH_3.COO^-]$ and $[H^+]$ stand for the *whole* concentrations of each of these ionic substances from *both* sources.

Now in normal acetic acid $[H^+] = 0.004$, $[CH_3.COO^-] = 0.004$, and $[CH_3.COOH] = 0.996$, practically 1. Substituting these values in the formula, we obtain:

$$\frac{0.004 \times 0.004}{1} = K \; (= 0.0_416).$$

When, however, ammonium acetate is dissolved in the liquid until the solution is also normal in respect to this substance, which may be considered as completely ionized in normal solution, the concentration of acetate-ion from this source is 1, and in the mixture of acid and salt, the small amount of acetate-ion furnished by the acid may be neglected, so that the *total* concentration of acetate-ion $[CH_3.COO^-]$ may be regarded as 1, or 250 times larger than in the acid alone. But the ionization constant K of acetic acid must recover its original value, and consequently $[H^+]$ must be diminished to something like $\frac{1}{250}$ of its former magnitude. That is, $[H^+]$ will become equal to about 0.000016,

$$\frac{0.000016 \times 1}{1} = K \; (= 0.0_416),$$

the rest of the hydrogen-ion uniting with a corresponding amount of acetate-ion to form molecular acetic acid. The concentration of this, however, increases thereby only from 0.996 to 0.999984; in other words, so much is already present that its concentration is practically unchanged. The chief effect of adding an equivalent amount of ammonium acetate therefore is, as we have seen, to reduce the concentration of hydrogen-ion below the amount (pH = 4; see p. 339) which can be detected by use of an indicator like methyl-orange.

Buffer Action. — Not only does ammonium acetate reduce the hydrogen-ion concentration of a solution of acetic acid to which it is added, but it also acts similarly when added to a solution of a *strong acid*, such as hydrochloric acid. As may be seen from the formulation:

$$\left.\begin{matrix} NH_4^+ + CH_3.COO^- \\ Cl^- \quad + \quad H^+ \end{matrix}\right\} \rightleftarrows CH_3.COOH$$

the union of H^+ and $CH_3.COO^-$ in the mixture will be almost complete.

Any salt of a weak acid will behave in this manner in the presence of a strong acid, and any salt of a weak base will likewise reduce the hydroxyl-ion concentration of a strong base. Thus if we add ammonium chloride to a solution of sodium hydroxide, we have:

$$\left.\begin{matrix} Na^+ + OH^- \\ Cl^- + NH_4^+ \end{matrix}\right\} \rightleftarrows NH_4OH.$$

Practical advantage is frequently taken of the above generalizations when it is desired to maintain the pH (see p. 338) of a solution at a constant value, the prohibitive effect of the added material upon any marked change in pH being known as **buffer action.** In a suitably buffered solution, we may have a reaction taking place which is slowly using up or producing an acid or a base, yet the pH of the solution remains practically unchanged. Even dilution has very little effect.

In the study of biochemistry, buffer solutions are particularly important. Human blood, for example, has a normal pH of 7.4, and a variation of only 0.4 on either side of this value involves fatal results. The absorption of acid or basic foods after a meal would exercise much more disagreeable effects than it does at present, therefore, if the blood did not contain salts which act as buffers.

Special Case of Saturated Solutions. — The commonest as well as the most interesting application of the conceptions developed above is met with in connection with saturated solutions, especially those of relatively insoluble substances.

The situation in a system consisting of saturated solution with excess of solute present has been discussed already (pp. 218–9),

but not from the ionic point of view. In considering electrolytes we shall first, for reasons which will become apparent below, take up the question on the basis of the Arrhenius theory of incomplete dissociation. In the case of silver chloride, for example, we have, according to the Arrhenius theory, the following scheme of equilibria:

$$\text{AgCl (solid)} \rightleftarrows \text{AgCl (undissociated in solution)} \rightleftarrows Ag^+ + Cl^-.$$

If we apply to the two reversible reactions represented in this scheme the principles which have been developed above, we obtain the two equations:

$$\frac{[\text{AgCl (undiss. in soln.)}]}{[\text{AgCl (solid)}]} = K_1 \qquad (1)$$

$$\frac{[Ag^+]\cdot[Cl^-]}{[\text{AgCl (undiss. in soln.)}]} = K_2 \qquad (2)$$

where K_1 and K_2 are the equilibrium constants of the two reactions. By multiplying equation (1) by equation (2), we obtain a third relationship:

$$\frac{[Ag^+]\cdot[Cl^-]}{[\text{AgCl (solid)}]} = K_1.K_2. \qquad (3)$$

Now [AgCl (solid)], the concentration of AgCl *in the solid state,* is invariable at any fixed temperature. Equation (3) consequently reduces to the form:

$$[Ag^+]\cdot[Cl^-] = K_1K_2\cdot[\text{AgCl (solid)}] = \text{a constant quantity.} \qquad (4)$$

In other words, **in a saturated solution, the product of the molar concentrations of the ions is a constant.** This product is called the **solubility product** of the substance. The **law** of the **constancy of the ion-product in a saturated solution** is one of the most useful of the principles of chemistry. It enables us to explain all the varied phenomena of precipitation and of the solution of precipitates in a consistent manner, as will be seen below. Upon the accuracy of the law of the constancy of the solubility product our whole system of quantitative analysis is based. It is of importance therefore to mention the fact that, although experimental test has shown that *both equation* (1) *and equation* (2) (see p. 327), by means of which the law was derived, *are grossly inaccurate for all strong*

electrolytes (neither K_1 nor K_2 remaining by any means constant as conditions are varied), yet for slightly soluble substances (see p. 758) *equation* (4), *the law itself, always approximates very closely to the truth.*

The question at once arises: How can two wrongs possibly make a right? Obviously only by one exactly compensating the other. We are led to suspect, therefore, that both equation (1) and equation (2) contain something which is not as it should be, and that by combining the two equations we eliminate this disturbing factor and bring everything correct again.

What have we eliminated? What do both equation (1) and equation (2) contain which is absent from equation (4)? Evidently the factor [AgCl (undissociated in solution)]. It is consequently *the undissociated fraction* of the electrolyte that is presumably responsible for the failure of the Arrhenius theory in the case of strong electrolytes, and we must study this undissociated fraction intensively if we wish to clear away the anomalies mentioned above.

Ellis Parker Butler wrote a short story once about a little black boy named Mose, who was persuaded by very good authority (namely, the word of the king of the ghosts, the general of the ghosts, the captain of the ghosts, etc.) of the fact that "Dey ain't no ghosts!" Similarly the net results of recent investigations on the undissociated molecule may be briefly summarized in the statement: "Dey ain't no undissociated molecule!" As we have already mentioned (p. 299), this is a slight exaggeration, but for strong electrolytes in aqueous solution it is, in general, essentially true.

Analysis of the derivation of the solubility product law confirms, therefore, our previous conclusion that the classical Arrhenius theory is inapplicable to strong electrolytes. For weak electrolytes, however, it is still perfectly valid (see p. 328).

Complete Ionization. — For any salt RX which is so slightly soluble that the activity coefficient (p. 279) of the ions may be considered equal to unity, the theory of complete ionization, which postulates the direct equilibrium: $R^+ + X^- \rightleftharpoons RX$ (solid), leads at once to precisely *the same condition for saturation:* $[R^+]\cdot[X^-] = K_{s.p.}$ (the solubility product constant) as was derived under the older hypothesis of Arrhenius. Under the modern theory, then, this important law is derived immediately without any complications. We now proceed to some experimental illustrations.

Illustration of the Principle of Solubility-Product Constancy. — When, to a **saturated** solution of one of the less soluble salts, a concentrated solution of a very soluble salt having **one ion in common** with the first salt is added, partial precipitation of the first salt is found to take place. This happens, for example, with a saturated solution of silver acetate, which is not very soluble (molar solubility 0.06 at 18°). The concentrations $[Ag^+]$ and $[C_2H_3O_2^-]$

being small, one may easily increase the value for one of the ions, say $[C_2H_3O_2^-]$, tenfold, by adding an acetate which is sufficiently soluble. To preserve the constancy of the product $[Ag^+] \times [C_2H_3O_2^-]$, the value of $[Ag^+]$ will then have to be diminished at once to approximately one-tenth of its former value. This can occur only, for a strong electrolyte, by withdrawal of ionic material from the solution; the residual nine-tenths of the $[Ag^+]$, together with an equivalent quantity of $[C_2H_3O_2^-]$, **will therefore be precipitated** as $AgC_2H_3O_2$. Hence the ionic concentration of a slightly soluble substance may be diminished and we may actually precipitate a considerable part of the dissolved material without introducing any substance which, in the ordinary sense, can interact with it.

In point of fact, when, to a saturated solution of silver acetate, there is added a concentrated solution of sodium acetate or of silver nitrate, a precipitate of silver acetate is thrown down.

Other Illustrations. — The precipitation of sodium chloride from a saturated solution, by the introduction of gaseous hydrogen chloride (p. 712), is to be explained, qualitatively at least (see below), in the same manner. The equilibria:

$$\downarrow NaCl\ (solid) \rightleftarrows Na^+ + Cl^-$$

are reversed by the introduction of additional Cl^- from the very soluble and highly ionized HCl.

The formation of potassium hydroxide by the interaction of potassium carbonate and calcium hydroxide (p. 699) ceases when a certain concentration has been reached. This occurs because the concentration of OH^-, which rapidly increases as the reaction proceeds, is a factor in the solubility product of calcium hydroxide. The larger $[OH^-]$ becomes, the less Ca^{++} is required to give the constant numerical value of this product. When the concentration $[Ca^{++}]$ from the hydroxide has become so small that the solubility product of calcium carbonate, $[Ca^{++}] \times [CO_3^{-}]$, is no longer exceeded, all motive for further interaction has been removed. The solubility product principle is thus as important in industrial operations as it is in analytical and other laboratory experimentation.

It must be understood that the above illustrations are presented with the object of providing the student with some practical and simple examples of the use of the solubility product principle, in order to make its significance and its importance immediately obvious. As a matter of fact, it may now

be added, to none of the cases discussed in the last two sections does the solubility product law apply *quantitatively*, and there are very good reasons why the agreement between experiment and theory should not be perfect except for much more slightly soluble substances.

We have already noted (for example, pp. 278, 327) that the simple law of molecular concentration is merely a limiting case, that attractive forces between the molecules may induce significant deviations therefrom, and that such attractive forces will be particularly evident in solutions containing electrically-charged ions. Unless the concentrations of the ions are very small indeed, therefore, activities and concentrations cannot be directly proportional, and the solubility product law must be modified by the introduction of the appropriate *activity coefficients* (p. 279). The magnitude of this correction is especially significant in the case of electrolytes containing polyvalent ions.

The above disturbing factor is a general one, and under the Debye-Hückel theory of complete ionization (p. 328) appropriate equations have been derived for each type of electrolyte (uni-univalent, uni-bivalent, uni-trivalent, bi-bivalent, etc.), which are too complex to be presented here, but which do express the actual solubility equilibria in normal cases *within the limits of experimental error*. We shall restrict ourselves, in the succeeding sections of this chapter, to examples where the simple law developed above may be assumed to apply directly. In certain systems, however, specific effects complicate the question still further, and we may discuss here two such factors very briefly.

The first, which becomes especially important in more concentrated solutions, is frequently called the *salting-out effect*. In view, however, of the use of this term in an entirely different connection in colloid chemistry (see p. 639), it may more appropriately be designated here the *dehydration factor*. For example, when concentrated sulphuric acid is dropped into a saturated solution of hydrochloric acid, using an apparatus similar to that shown in Fig. 94 (p. 224), a steady stream of hydrogen chloride gas is evolved. This affords, in fact, one of the most convenient means of preparing the gas in the laboratory. It would be erroneous, however, to assume that the evolution of the gas is regulated entirely by the repression of the ionization of the hydrochloric acid by the sulphuric acid:

$$H^+ + Cl^- \rightleftharpoons HCl \text{ (dissolved)} \rightleftharpoons HCl \text{ (gas)} \uparrow.$$

A much more potent factor here is the **removal of solvent water** by the sulphuric acid through the formation of hydrates. This removal of solvent automatically converts the already saturated solution of HCl into a supersaturated one, and gas is therefore evolved until equilibrium is again attained. Since HCl also combines with water to form hydrates in solution, this same *dehydration factor* plays a part in the precipitation of sodium chloride from a saturated solution by the introduction of gaseous hydrogen chloride (see p. 757).

The second factor is the *formation of definite compounds* between the insoluble salt and the added electrolyte. Thus, when we add sodium chloride to a saturated solution of silver chloride in water, the solubility is *not* diminished, although we may have increased the concentration of chloride ion in the solution many thousand times. As a matter of fact, silver chloride is much more soluble in a concentrated solution of sodium chloride than it is in pure water (see p. 807). Similarly, barium sulphate is much more soluble in a very

concentrated solution of sulphuric acid than it is in pure water (p. 738). The explanation is similar to that given in an earlier chapter for the increase in the solubility of iodine in water on addition of potassium iodide (p. 350). The simple salt, with which the solution is originally saturated, is largely removed as such from the solution by the added substance, and exists therein instead mainly as part of a *molecular compound* or part of a *complex ion*. How the magnitude of the effect depends upon the stability of such complexes is a matter which will be considered in detail in a later chapter (pp. 788–9).

Precipitation by Double Decomposition. — The mechanism of this type of reaction has already been discussed in some detail in an earlier chapter (p. 329), to which reference should here be made by the reader. The solubility-product law, however, throws much additional light on the subject, and enables us to forecast the *completeness* of any given precipitation under given conditions.

The first thing to be remembered is that the precipitate which we observe, however insoluble its material may be, does not include *all* of the substance, but only the excess beyond what is required to saturate the water. **The liquid surrounding the precipitate is always a saturated solution of the substance precipitated.** If it were not so, some of the precipitate would dissolve until the liquid became saturated. Thus, for example, when we add ammonium sulphide solution to zinc chloride solution (p. 749),

$$\left.\begin{matrix} 2NH_4^+ + S^= \\ 2Cl^- \quad + Zn^{++} \end{matrix}\right\} \rightleftarrows ZnS\downarrow$$

the resultant liquid is a saturated solution of zinc sulphide, with the excess of this salt suspended in it as a precipitate.

Looking at the matter from this viewpoint, we perceive the application of the rule of solubility-product constancy. In this *saturated* solution the product of the ion-concentrations, $[Zn^{++}] \times [S^=]$, is constant. If the original solutions had been so very dilute that, when they were mixed, the product of the concentrations of these two ions had *not* reached the value of this constant, *no precipitation would have occurred.* As a matter of fact, the solubility-product of zinc sulphide is so small (approximately 1×10^{-24}) that in all ordinary mixtures the product $[Zn^{++}] \times [S^=]$ considerably exceeds the requisite value, and hence the salt is thrown down until the balance remaining gives the value in question. The **rule for precipitation,** then, is as follows: **Whenever the product of the concentrations of any two ions in a mixture exceeds the value of the ion-product in a saturated solution of the compound formed by their union, this compound will be precipi-**

tated. Naturally the substances with small solubilities, and therefore small solubility-product constants, are the ones most frequently formed as precipitates.

The approximate solubility-product values for a few typical salts at 18° are given below.

Silver acetate	4×10^{-3}	Silver bromide	1×10^{-13}
Calcium sulphate	6×10^{-5}	Silver iodide	1×10^{-16}
Calcium oxalate	1×10^{-9}	Cadmium sulphide	4×10^{-29}
Barium sulphate	1×10^{-10}	Cupric sulphide	1×10^{-42}
Silver chloride	1×10^{-10}	Silver sulphide	1×10^{-49}

Completeness of Precipitation. — In the case of zinc sulphide, we may precipitate the salt practically completely from solution by adding *excess* of ammonium sulphide. It is true that this substance (see p. 709) is highly hydrolyzed in solution, but still a solution which contains it in excess contains a significant concentration of sulphide ion $S^{=}$. The amount of zinc ion Zn^{++} that can exist simultaneously in such a solution is negligible, since otherwise the solubility-product of zinc sulphide would be exceeded. *Zinc is therefore precipitated quantitatively as zinc sulphide by addition of excess of ammonium sulphide to a solution of any zinc salt.* This is a fact which is turned to practical use in quantitative analysis.

If we attempt to carry out the precipitation with hydrogen sulphide instead of ammonium sulphide, however, we find that only partial precipitation of the zinc as sulphide occurs (p. 749). However great an excess of H_2S we add, precipitation is *incomplete.* The reason for this is immediately apparent from a study of the full ionic equations:

$$\left.\begin{array}{r} H_2S \rightleftarrows 2H^+ + S^= \\ 2Cl^- + Zn^{++} \end{array}\right\} \rightleftarrows ZnS\downarrow.$$

Hydrogen sulphide is so slightly ionized in solution that the concentration of sulphide ion $S^{=}$ that it supplies is extremely small (see p. 405). A large amount of zinc ion Zn^{++} can therefore remain in solution without the solubility-product of zinc sulphide being exceeded.

Rule for Solution of Substances. — The **rule for solution** of any electrolyte follows at once from the foregoing considerations, and may be formulated by changing a few of the words in the rule just given: **Whenever the product of the concentrations of any two ions in a mixture *is less than* the value of the ion-product in a**

saturated solution of the compound formed by their union, this compound, if present in the solid form, **will be *dissolved*.** When applied to the simplest case, this rule means that a substance will dissolve in a liquid not yet saturated with it, but will not dissolve in a liquid already saturated with the same material. The main value of the rule lies, however, in its application to the less simple, but equally common cases, when an ordinarily insoluble body is brought into solution by interaction with another electrolyte.

Applications of the Rule: Solution of Insoluble Substances. — So long as a substance remains in pure water its solubility is fixed. Thus, with calcium hydroxide, the system comes to equilibrium at 18° when 0.17 g. per 100 c.c. of water (0.02 moles per liter) have gone into solution:

$$Ca(OH)_2(\text{solid}) \rightleftarrows Ca^{++} + 2OH^-.$$

But if an additional reagent which can combine with either one of the ions is added, the concentration of this ion at once becomes less, the actual numerical value of the ion-product therefore begins to diminish, and further solution must take place to restore its value. Thus, if a little of an acid (giving H^+) be added to the solution of calcium hydroxide, the union of OH^- and H^+ to form water removes almost all the OH^- (see p. 338), and solution of the hydroxide proceeds until the acid is used up. There are now far more Ca^{++} than OH^- ions present, but solution of the hydroxide continues until the *ion-product* reaches the same value as before, and then (and only then) equilibrium is re-established. If a further supply of acid is added, the removal of OH^- to form H_2O begins again. Hence, with excess of acid, the calcium hydroxide finally all dissolves.

This particular action is a neutralization of an insoluble base. But the other kinds of actions by which insoluble electrolytes pass into solution all resemble it closely, and differ only in details. The general outlines of the explanation are the same in every case. We proceed now to apply it to the common phenomenon of the solution of an insoluble salt by an acid.

Interaction of Insoluble Salts with Acids, Resulting in Solution of the Salt. — Zinc sulphide passes into solution when in contact with acids, especially strong acids. Thus, with hydrochloric acid, it gives zinc chloride and hydrosulphuric acid (compare p. 409):

$$ZnS + 2HCl \leftrightarrows ZnCl_2 + H_2S. \qquad (1)$$

The action of acids upon insoluble salts is so frequently mentioned in chemistry and is so important a factor in analytical operations that it demands separate discussion. This example is a typical one and may be used as an illustration.

According to the rules already explained (pp. 759–61), zinc sulphide is precipitated when the numerical value of the product of the concentrations of the two requisite ions, $[Zn^{++}] \times [S^{=}]$, exceeds the value of the ion-product for a saturated solution of zinc sulphide in pure water. When, on the contrary, the product of the concentrations of these two ions falls below the limiting value, a condition which may arise from the removal in some way either of the Zn^{++} or of the $S^{=}$ ions, the solid will dissolve to replace them until the ionic concentrations necessary for equilibrium have been restored or until the whole of the solid present is consumed. Here the sulphide-ion from the zinc sulphide combines with the hydrogen-ion of the strong acid HCl which has been added, and forms molecular H_2S:

$$S^{=} + 2H^{+} \leftrightarrows H_2S. \qquad (2)$$

It will be seen that the removal of the ions in this fashion can result in considerable solution of the salt only when the acid produced is a feebly ionized one. Here, to be specific, the concentration of the $S^{=}$ in the hydrosulphuric acid equilibrium (2) above must be less than that of the same ion in a saturated zinc sulphide solution. Now hydrosulphuric acid belongs to the least active class of acids, and its pure solution contains only a very small concentration of $S^{=}$ (p. 405). There is, however, another factor in the situation which we have not yet taken into account. The hydrochloric acid which we used for dissolving the precipitate is a very highly ionized acid and gives an enormously greater concentration of hydrogen-ion than does hydrosulphuric acid. Hence the hydrogen-ion is in large excess in equation (2), and the condition for equilibrium, $\frac{[H^{+}]^2 \times [S^{=}]}{[H_2S]} = K$, will be satisfied by a correspondingly much smaller concentration of $S^{=}$. In this particular case, therefore, the $[S^{=}]$ of the hydrosulphuric acid *is* far less than that given by the zinc sulphide. The whole change, evidently, depends for its accomplishment, not only on the mere presence of hydrogen-ion, but *on the repression of the ionization of the hydrosulphuric acid* by the great excess of hydrogen-ion furnished *by the strong*

acid that has been used. The complete scheme of the equilibria is as follows:

$$\left.\begin{array}{lll}\downarrow ZnS\ (solid) \leftrightarrows & Zn^{++} & + S^{=} \\ & 2Cl^{-} & + 2H^{+}\end{array}\right\} \leftrightarrows \begin{array}{c}H_2S \\ (dissolved)\end{array} \rightleftarrows \begin{array}{c}H_2S\uparrow \\ (gas)\end{array}$$

A **generalization** may be based on these considerations: **an insoluble salt of a given acid will in general interact and dissolve when treated with a solution containing another acid, provided that the latter acid is a much more highly ionized (more active) one than the former.**

Precipitates Insoluble in Acids. — But even strong acids frequently fail to bring salts of weak acids into solution. Here the cause lies in the fact that such salts are far less soluble than those of the zinc sulphide type. Thus, even hydrochloric acid (normal) will not appreciably dissolve cupric sulphide. The solubility product $[Cu^{++}] \times [S^{=}]$ for this salt is so small (1×10^{-42}) that, after an infinitesimal amount has gone into solution, the sulphide-ion concentration is sufficient, in spite of the repressive action of the large hydrogen-ion concentration furnished by the HCl, to bring the product $[Cu^{++}] \times [S^{=}]$ up to its maximum possible value. In this case the first link in the chain of equilibria:

$$\left.\begin{array}{lll}\downarrow CuS\ (solid) \leftrightarrows & Cu^{++} & + S^{=} \\ & 2Cl^{-} & + 2H^{+}\end{array}\right\} \leftrightarrows \begin{array}{c}H_2S \\ (dissolved)\end{array} \rightleftarrows \begin{array}{c}H_2S\uparrow. \\ (gas)\end{array}$$

furnishes Cu^{++} and $S^{=}$ with such hesitancy that only the use of very concentrated acid will increase the concentration of the H^{+} to an extent sufficient to secure a significant advance of the whole action. We must add, therefore, to the above rule: **provided also that the salt is not one of extreme insolubility.**

Illustrations of the application of these generalizations are countless. Carbonic acid is made from marble (p. 564), hydrogen sulphide from ferrous sulphide (p. 402), hydrogen peroxide from sodium peroxide (p. 367), and phosphoric acid from calcium phosphate (p. 552). In each case the acid employed to decompose the salt is stronger than the acid to be liberated. On the other hand, calcium phosphate is *insoluble* in acetic acid because this acid is weaker than is phosphoric acid. We have thus only to examine the list of acids showing their degrees of ionization (p. 317) in order to be able to tell which salts, if insoluble in water, will be dissolved by acids and, in general, what acids will be sufficiently active in each case for the purpose. In

chemical analysis we discriminate between salts soluble in water, those soluble in acetic acid (the insoluble carbonates and some sulphides, FeS and MnS, for example), those requiring strong acids for their solution (calcium phosphate, zinc sulphide and the more insoluble sulphides, for example), and those insoluble in all acids (barium sulphate and other insoluble salts of strong acids).

The influence of solubility is shown not only by the sulphides, but also, for example, by the sulphates. Thus, barium sulphate is not appreciably dissolved even by the most active acids (p. 738), being a salt of a rather highly ionized acid, and being itself very insoluble. Yet calcium sulphate, being much less insoluble (p. 720), is dissolved to a noticeable extent by the same acids.

Precipitation of Insoluble Salts in Presence of Acids. — The **converse of solution,** namely, **precipitation,** depends of course upon precisely the same conditions: **an insoluble salt which is dissolved by a given acid cannot be formed by precipitation in the presence of this acid.** Thus calcium phosphate or sulphide can be precipitated in presence of acetic acid, but not in presence of strong acids in ordinary concentrations. Cupric sulphide or barium sulphate can be precipitated in presence of any acid, but ferrous sulphide and calcium carbonate only in the absence of acids.

From this it does not follow that zinc sulphide, for example, cannot be precipitated if once a strong acid has been added to the mixture. To secure precipitation, all that is necessary is to remove the excess of hydrogen-ion which is repressing the ionization of the hydrosulphuric acid. This can be done by adding a base, by adding ammonium sulphide, or even by adding excess of sodium acetate. The acetate-ion $C_2H_3O_2^-$ removes practically all the H^+ to form the little ionized acetic acid (compare p. 754), and $[S^=]$ consequently increases to a point where zinc sulphide can be precipitated.

Exercises. — 1. (*a*) How do the electrolytic methods of making calcium and magnesium differ? (*b*) Why not electrolyze an aqueous solution of magnesium chloride in making magnesium? (*c*) Why use both calcium and sodium chlorides in making magnesium? (*d*) Why is magnesium, but not calcium or sodium, liberated?

2. Why are magnesium and zinc not found free in nature?

3. Why does magnesium rust completely (in time), while zinc does not?

4. Make equations for: (*a*) the action of magnesium on hydrochloric acid; (*b*) the burning of magnesium in air; (*c*) the heating of magnesium carbonate; (*d*) the precipitation of magnesium hydroxide from the sulphate; (*e*) the hydrolysis of magnesium chloride.

5. Why is salt containing magnesium chloride, after mixing with sodium bicarbonate, no longer deliquescent?

6. Make equations for: (*a*) the action of hydrogen sulphide on zinc oxide; (*b*) the precipitation of zinc hydroxide; (*c*) the action of sodium hydroxide on zinc hydroxide.

7. What will be the effect of adding a concentrated solution of silver nitrate to a saturated solution of silver sulphate (see table of solubilities)?

8. Write full ionic equations for the reactions mentioned on p. 763.

9. Show, by means of ionic equations, why it is possible to prevent the precipitation of magnesium hydroxide when ammonium hydroxide is added to a soluble magnesium salt, by prior addition of ammonium chloride. (Use pp. 752–4.)

10. Why is it not possible, in the same way, to prevent the precipitation of magnesium hydroxide when sodium hydroxide is added to a soluble magnesium salt, by prior addition of sodium chloride?

11. Magnesium hydroxide is soluble only to the extent of 0.001 g. in 100 c.c. of water at 18°. Why does the addition of a few c.c. of dilute hydrochloric acid to precipitated magnesium hydroxide bring it practically immediately into solution? Formulate ionically.

12. From an inspection of the solubility data for the oxalates on the inside front cover, would you infer that the precipitation of magnesium oxalate MgC_2O_4 by the addition of ammonium oxalate to a soluble salt of magnesium could be prevented by prior addition of ammonium chloride in excess?

13. When an electric current is passed through a concentrated solution of cadmium iodide, it appears that *both* cadmium *and* iodine migrate towards the positive electrode. Explain (p. 750).

14. What would be the effect of mixing equivalent amounts of zinc chloride and sodium zincate solutions? Test your conclusion experimentally and formulate the ionic reactions.

15. Explain in detail why calcium oxalate is soluble in hydrochloric acid, but not in acetic acid.

16. What reagent would you use to precipitate cadmium sulphide quantitatively from a solution of cadmium chloride? Justify your choice.

17. From an inspection of the solubility table of the sulphates on the inside front cover, would you infer that a precipitate of strontium sulphate, formed by addition of a saturated solution of calcium sulphate to a solution of strontium chloride, would be soluble in concentrated hydrochloric acid? Test your inference experimentally.

18. Saturated solutions of barium hydroxide and calcium sulphate at 18° are mixed together. Of what does the precipitate consist? How would you proceed to confirm your conclusion?

19. On p. 753, it was assumed that ammonium acetate was completely ionized in aqueous solution. In actual fact, since it is a salt of a weak acid and a weak base, it is hydrolyzed to the extent of about one-half of one per cent. Formulate the complete equations for the hydrolysis and explain why the solution, in spite of this, still reacts essentially neutral.

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CHAPTER XLV

ALUMINIUM AND THE RARE EARTH METALS

The family of trivalent elements to which the metal aluminium belongs includes the non-metal boron (p. 666), and a number of rare metals. On the right hand side of the fourth column of the periodic table we have **aluminium** (Al, atomic number 13), **gallium** (Ga, at. no. 31), **indium** (In, at. no. 49), and **thallium** (Tl, at. no. 81). On the left hand side there are **scandium** (Sc, at. no. 21), **yttrium** (Yt, at. no. 39) and **lanthanum** (La, at. no. 57). Lanthanum is immediately followed in the periodic system by the remaining **metals of the rare earths,** fourteen in number (at. nos. 57–71), the similarity in the chemical properties of which has already been discussed from the view-point of atomic structure on p. 499.

The Rare Elements of This Family. — Gallium and **indium** occur occasionally in zinc-blende, and were discovered by the use of the spectroscope. The former takes its name from the country (France) in which the discovery was made, and the latter from two blue lines shown by its spectrum. Indium gives a complete series of compounds in which it is trivalent, and the chlorides $InCl$ and $InCl_2$ are also known.

Thallium is found in some specimens of pyrite and blende. It was discovered by Crookes, by means of the spectroscope, in the seleniferous deposit from the flues of a sulphuric acid factory. It received its name from the prominent green line in its spectrum (Greek, θαλλός, a green twig). It gives two complete series of compounds. In those in which it is trivalent (thallic salts), it resembles aluminium. Univalent thallium recalls both sodium and silver. Thallous hydroxide $TlOH$ is soluble, and gives a strongly alkaline solution, but the chloride is insoluble in cold water. The solutions of the thallous salts are neutral. The metal is displaced from its salts by zinc.

Of the elements on the left side of the column, **scandium** (at. no. 21), whose existence and properties were predicted by Mendelejeff (p. 448), is the best known. The metals of the **rare earths,** of

which **lanthanum** (at. no. 57) is one, are found in minerals such as euxenite, gadolinite, orthite, and monazite, which occur in Sweden, Greenland, and the United States. **Cerium** (Ce, at. no. 58, see also p. 836), **praseodymium** (Pr, at. no. 59), and **neodymium** (Nd, at. no. 60) occur along with **lanthanum** in cerite, a silicate of these four elements.

The rare earth elements are distinguished by the extraordinary similarity of their chemical and most of their physical properties, a fact which renders their separation a matter of extreme difficulty. It is necessary, in practice, to take advantage of slight differences in solubility observed for corresponding salts and to resolve a given mixture into its components by a long series of fractional crystallizations or precipitations, ranging in number from several hundred to many thousand according to the elements present and the degree of purity desired. These operations are so laborious and time-consuming that chemically pure samples of individual rare earth compounds are practically unknown, save on the shelves of a few skilled workers in the field of atomic weights. The "rareness" of the rare earths is due not so much to the lack of abundance of their ores in nature as to the lack of a simple method for their separation.

It has been shown lately that a much more rapid separation may be effected in certain mixtures by taking advantage of the fact that the ionic mobilities (p. 315) of the various trivalent metal cations are not identical. When a short section of a mixed solution is made to travel a long distance along a tube by the electric current (compare Fig. 109, p. 311), the faster ion accumulates in the front half of the section and the slower ion in the rear. Even adjacent members of the group, such as praseodymium and neodymium, may be separated by this method.

It is of interest to note that, until recently, there was a blank space in the rare earth family, the element with atomic number 61 not being known to chemists. In the spring of 1926, the X-ray spectrum lines of this element (compare Fig. 133, p. 474) were recognized by Professor Hopkins of the University of Illinois in the end fractions from neodymium and samarium residues. The new element has been named by its discoverer **illinium**, with the symbol Il.

In 1932, it was discovered by Hevesy and Pahl that **samarium** was very faintly **radioactive**, emitting alpha-particles, with a half-life period of about 1×10^{12} years.

ALUMINIUM Al

The Chemical Relations of the Element. — Aluminium is trivalent exclusively. Its hydroxide, like that of zinc (p. 748), is **amphoteric**, that is to say, it is feebly acidic as well as basic, and hence the metal forms two sets of compounds of the types $NaAlO_2$ (sodium meta-aluminate) and $Al_2(SO_4)_3$. The salts of both series are more or less hydrolyzed by water, the former very conspicuously so. It is worth noting that the hydroxides of the trivalent

metals, or metals in the trivalent condition, such as $Al(OH)_3$, $Cr(OH)_3$, $Fe(OH)_3$ are all distinctly less basic than are those of the bivalent metals such as $Zn(OH)_2$, $Cd(OH)_2$, $Fe(OH)_2$, $Mn(OH)_2$. This fact is **used in analysis** (see also p. 919) in separating the two sets. When a solution of the chlorides is shaken with precipitated barium carbonate, the free acid from the more highly hydrolyzed salts of Al^{+++}, Cr^{+++}, and Fe^{+++} interacts with this substance, the hydrolysis is promoted:

$$AlCl_3 + 3H_2O \rightleftarrows Al(OH)_3 + 3HCl,$$

and eventually the hydroxides $Al(OH)_3$, $Cr(OH)_3$, and $Fe(OH)_3$ are completely precipitated. The chlorides of the bivalent metals remain in the solution.

Aluminium does not enter into complex anions or cations. In this is differs from zinc and resembles magnesium. It is too feebly base-forming to give salts like the carbonate or sulphide, because hydrolysis causes precipitation of the hydroxide (p. 682).

Occurrence. — Aluminium is found very plentifully in combination, coming next to oxygen and silicon in this respect. The **feldspars** (such as $KAlSi_3O_8$), the **micas** (such as $KAlSiO_4$), and **kaolin** (clay) $H_2Al_2(SiO_4)_2,H_2O$ are the commonest minerals containing it. Since the soil has been formed largely by the weathering of minerals like the feldspars, clay and other products of the decomposition of such minerals constitute a large part of it. **Garnets,** which are found in metamorphic rocks, are mainly an orthosilicate of calcium and aluminium $Ca_3Al_2(SiO_4)_3$. **Turquoise** is a hydrated phosphate $Al_2(OH)_3PO_4,H_2O$, and **cryolite** a double fluoride $3NaF,AlF_3$. Various forms of the oxide and the hydroxide are also found. **Bauxite** ($Al_2O_3,2H_2O$) is a valuable hydrated oxide.

Manufacture and Physical Properties. — The making of aluminium on a large scale originated in C. M. Hall's discovery (1886) that the oxide could be electrolyzed in solution in molten cryolite. Iron tanks (Fig. 205) are lined with a compressed mixture of coke and tar which is afterwards baked. This carbon lining forms the cathode, while the anodes consist of a series of rods of carbon about 3 inches in diameter which are attached to copper clamps. The cryolite is first melted (1000°) by the arcs struck by the carbon rods when the current is applied. The anodes are then raised somewhat, the aluminium oxide is added, and some coal (which floats) is thrown

in to cover the surface and obscure the blinding glow due to the liberation of oxygen at the carbon anodes. From time to time more of the oxide is added and the melted aluminium is tapped off from the floor of the cell. Fifty years ago the whole world's production was only about 40 kilograms a year. In 1935 the United States alone produced 54,000 metric tons, the world's production being approximately 260,000 metric tons. The price has fallen, during the same period, from 15 dollars to 20 cents per pound.

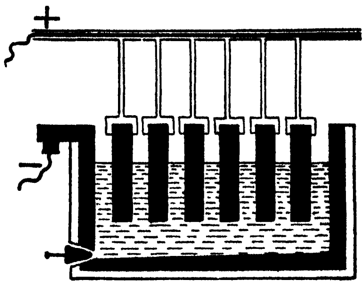


FIG. 205. Manufacture of Aluminium.

The metal melts at 660°, but is not mobile enough to make castings. It is exceedingly light (sp. gr. 2.6), and in tensile strength excels the other metals, with the exception of iron and copper. It is malleable, and the foil is taking the place of tin foil for wrapping foods. It has a silvery luster, and tarnishes very slightly, the *firmly adhering* film of oxide first formed protecting its surface. Although, comparing cross-sections, it is not so good a conductor of electricity as is copper, yet *weight for weight* it conducts better. It is difficult to work on the lathe or to polish, because it sticks to the tools, but the alloy with magnesium (about 2 per cent) called **magnalium** has admirable qualities in these respects. **Aluminium bronze** (5–12 per cent aluminium with copper) is easily fusible, has a magnificent golden luster, and possesses mechanical and chemical resistance exceeding that of any other bronze. The metal and its alloys are used for making cameras, opera-glasses, cooking utensils, the metal parts of dirigibles and aeroplanes, and other articles requiring lightness and strength, as well as for the transmission of electricity. The powdered metal, mixed with oil, is used in making a silvery paint.

Chemical Properties. — The metal displaces hydrogen from hydrochloric acid very easily. In sulphuric or nitric acid, however, it receives a coating of the hydroxide, formed by hydrolysis of the salt, and the action is slow in the former case, and almost nil in the latter. It liberates hydrogen also from boiling solutions of the alkalies, forming meta-aluminates:

$$2Al + 2NaOH + 2H_2O \rightarrow 2NaAlO_2 + 3H_2.$$

In consequence of its very great affinity for oxygen, aluminium displaces from their oxides the metals below it in the electromotive series. Thus, when a mixture of aluminium powder and ferric oxide (**thermite**) is placed in a crucible and ignited by means of a piece of burning magnesium ribbon, aluminium oxide and iron are formed:

$$Fe_2O_3 + 2Al \rightarrow Al_2O_3 + 2Fe.$$

A temperature of 3000° to 3500° is produced by the action, the molten iron (m.-p. above 1500°) collects at the bottom, and the immiscible molten aluminium oxide (m.-p. 2050°) floats to the top. This very simple method of making pure specimens of metals like chromium, uranium, and manganese, whose oxides are otherwise hard to reduce, is called by Goldschmidt, the inventor, **aluminothermy.** By preheating the ends of steel rails with a gasoline torch, firing a mass of thermite in a crucible above the joint, and allowing the iron to flow into the joint, perfect welds are made. In the same way, large castings, like propeller shafts, when broken, can be mended. The sulphides, such as pyrite, are reduced with like vigor by aluminium.

A very large part of the aluminium of commerce is used by steelmakers. When added in small amount (less than 1 : 1000) to molten steel, it combines with the gases, and gives sound ingots free from blow holes.

Aluminium Chloride $AlCl_3$. — If the metal or the hydroxide is treated with hydrochloric acid, and the solution is allowed to evaporate, crystals of $AlCl_3,6H_2O$ are formed. When heated, this hydrate is completely hydrolyzed, hydrochloric acid is given off, and only the oxide remains. The **anhydrous chloride** is much used as a catalytic agent for causing combination in organic chemistry. It is made on a large scale by passing chlorine at 850° over an intimately powdered mixture of calcined bauxite and coke:

$$Al_2O_3 + 3C + 3Cl_2 \rightarrow 2AlCl_3 + 3CO.$$

Aluminium chloride gives a vapor pressure of 760 mm. at 183°, and sublimes, as a white crystalline solid, without melting. Under pressure, it melts at 193°. In the mode of preparation described above, it is, therefore, vaporized, and condenses in a cool part of the tube. It fumes when exposed to moist air, on account of the hydrogen chloride produced by hydrolysis; and only with excess of hydrochloric acid does it give a clear solution free from basic salts.

Aluminium Hydroxide $Al(OH)_3$. — The hydroxide is precipitated when ammonium hydroxide, or other alkaline hydroxide, is added to a solution of a salt of aluminium:

$$Al_2(SO_4)_3 + 6NH_4OH \rightarrow 2Al(OH)_3 \downarrow + 3(NH_4)_2SO_4.$$

It loses water gradually when dried, without forming any intermediate hydroxides (compare p. 662), until Al_2O_3 alone remains. Natural forms of this substance are **hydrargyllite** $Al(OH)_3$ ($= Al_2O_3,3H_2O$), **bauxite** $Al_2O(OH)_4$ ($= Al_2O_3,2H_2O$), which always contains ferric oxide, and **diaspore** $AlO.OH$ ($= Al_2O_3,H_2O$).

Commercially, the hydroxide is made by heating bauxite with dry sodium carbonate, or with concentrated sodium hydroxide solution at 150–170°. The ferric oxide, having no tendency to form a carbonate or to interact with a base, remains unchanged. The sodium meta-aluminate which is formed is extracted with water:

$$Al_2O(OH)_4 + Na_2CO_3 \rightarrow 2NaAlO_2 + CO_2 + 2H_2O.$$

The hydroxide is then precipitated by passing carbon dioxide through the solution:

$$2NaAlO_2 + CO_2 + 3H_2O \rightarrow Na_2CO_3 + 2Al(OH)_3.$$

It tends to remain in colloidal suspension (p. 641), and forms a *white gelatinous precipitate*. It is *both weakly basic* and *feebly acidic* in chemical properties. In acids it dissolves forming salts of aluminium, such as the chloride $AlCl_3$ or sulphate $Al_2(SO_4)_3$. Solutions of these salts in water give an acid reaction, owing to hydrolysis (p. 681).

Aluminium hydroxide, as a weak acid, interacts only slightly with ammonium hydroxide, because this substance is too feebly basic, but it dissolves readily in sodium hydroxide solution, to form **sodium meta-aluminate** $NaAlO_2$:

$$NaOH + H_3AlO_3 \rightleftarrows NaAlO_2 + 2H_2O.$$

The meta-aluminates are extensively hydrolyzed by water, and their solutions have a strong *alkaline* reaction.* Hence an excess

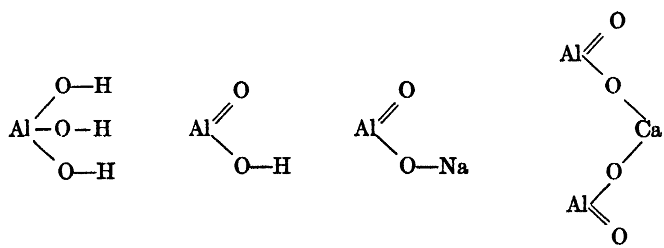
* Ortho-aluminates of the type Na_3AlO_3 apparently do not exist. The meta-aluminates are derived from the hypothetical acid $HAlO_2$ ($= H_3AlO_3 - H_2O$, compare p. 662).

of sodium hydroxide is required for the complete solution of aluminium hydroxide. Sodium aluminate is used as a mordant in dyeing (see p. 648), on account of the ease with which the solution gives up aluminium hydroxide when any material is present which can adsorb the free portion of the hydroxide and so cause backward displacement of the above equilibrium.

When calcium chloride is added to a solution of sodium aluminate, the insoluble **calcium meta-aluminate** is deposited:

$$2NaAlO_2 + CaCl_2 \rightarrow Ca(AlO_2)_2 + 2NaCl.$$

The relations of all these substances are shown by the following formulæ (compare p. 551):



A number of insoluble meta-aluminates are found in nature. They crystallize in the regular system, and are known as **spinelles.** They contain bivalent metals in place of the calcium in the last-named compound. Thus we have **spinelle** proper $Mg(AlO_2)_2$, and **gahnite** $Zn(AlO_2)_2$. Corresponding and isomorphous derivatives of chromic and ferric hydroxides are **chromite** $Fe(CrO_2)_2$ and **magnetite** $Fe(FeO_2)_2$.

Aluminium hydroxide, precipitated from the sulphate, is used in purifying water (p. 775). It is employed also in **sizing** cheaper grades of **paper** (p. 600), an operation required to prevent the absorption and consequent spreading of the ink. For writing-paper, gelatine solution is employed. In making printing-papers, rosin soap (made by dissolving rosin in caustic soda) is mixed with the paper-pulp, and aluminium sulphate is added. The rosin and aluminium hydroxide are precipitated in the pulp, and pressing between hot rollers afterwards melts the former and gives a surface to the paper.

Delicate cloth goods are rendered waterproof by saturating them with aluminium acetate solution and then steaming them to promote hydrolysis. The aluminium hydroxide is thus precipitated in

the capillaries of the cotton or linen and renders them non-absorbent:

$$Al(CO_2CH_3)_3 + 3H_2O \rightleftarrows Al(OH)_3 + 3HCO_2CH_3.$$

Aluminium Oxide Al_2O_3. — The oxide (**alumina**) is made by heating the pure hydroxide made from bauxite (see p. 771). It is found in nature in pure form as **corundum.** This mineral is only one degree less hard than the diamond. **Emery** is a common variety, contaminated with ferric oxide, and was widely used as an abrasive until largely displaced by carborundum. The sapphire is pure aluminium oxide tinted by a trace of a compound of chromium, while the ruby is the same material colored with aluminates of iron and titanium. By allowing the pulverized oxides to be carried by the stream of oxygen of an oxy-hydrogen blowpipe, and placing a disc in the flame to catch the molten particles, "synthetic" sapphires to the extent of six million carats and synthetic rubies to the extent of ten million carats are now made annually. The artificial gems are chemically identical with the natural ones, and can be distinguished only by the fact that they are free from microscopic bubbles and other defects. **Alundum,** an artificial abrasive, also used as a refractory material for crucibles and muffles, is made by barely melting the oxide in the electric furnace.

The alumina made by gently heating the hydroxide interacts easily with acids, but after being strongly heated it resembles natural alumina in being very slowly affected by them. Minerals containing insoluble compounds of aluminium are attacked when heated strongly with potassium bisulphate (compare p. 705), the sulphate of aluminium being formed.

Aluminium Sulphate. — **Aluminium sulphate** $Al_2(SO_4)_3,18H_2O$ is prepared by treating either bauxite or pure clay (kaolin) with sulphuric acid. In the latter case the insoluble residue of silicic acid is removed by filtration:

$$H_2Al_2(SiO_4)_2 + 3H_2SO_4 \rightarrow Al_2(SO_4)_3 + 2H_4SiO_4\downarrow.$$

The solution of the sulphate is acid in reaction. It crystallizes in leaflets which, when the source was clay or bauxite, have a yellow tinge due to the presence of iron as an impurity. The salt is used (see Fig. 206) as a source of precipitated aluminium hydroxide in paper-making, water purification, and dyeing.

Alums. — When aluminium sulphate and potassium sulphate are dissolved together in equi-molecular proportions, the solution deposits transparent octahedral (Fig. 18, p. 60) crystals of hydrated potassium-aluminium sulphate $K_2SO_4,Al_2(SO_4)_3,24H_2O$. Potassium-aluminium sulphate is a *double salt*, and is one of a large class known as the **alums.** The alums have the general formula $M_2^{I}SO_4,M_2^{III}(SO_4)_3,24H_2O$, and may be made as above by using a sulphate of a univalent metal with one of a trivalent metal. Thus, for M^{I} we may use K, NH_4, Rb, Cs, and Tl^{I}, and for M^{III}, Al, Fe^{III}, Cr^{III}, Mn^{III}, and Tl^{III}. We may even employ selenates, such as K_2SeO_4. All of the resulting double salts are isomorphous, and a crystal of one will continue to grow in a solution of another, acquiring, of course, an outer layer of different composition, but of the same crystallographic orientation (see p. 691).

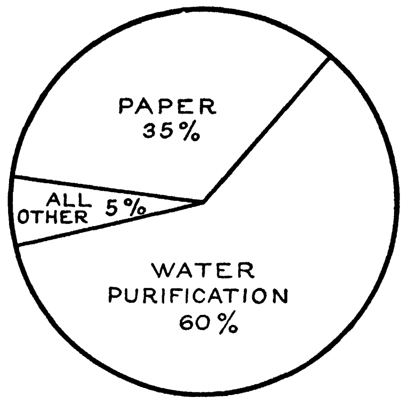


FIG. 206. Distribution of Aluminium Sulphate in Industry.

Potassium-aluminium sulphate is also prepared by heating **alunite,** a basic alum found near Rome and in Hungary, and extracting the product with hot water. The alunite, having the composition $KAl_3(OH)_6(SO_4)_2$, leaves an insoluble residue of the hydroxide, mixed with ferric oxide which is present as an impurity:

$$2KAl_3(OH)_6(SO_4)_2 \rightarrow K_2SO_4,Al_2(SO_4)_3 + 4Al(OH)_3.$$

The saturated solution of potash alum contains, at 10°, 9 parts of the anhydrous salt in 100 parts of water, and at 100°, 422 parts in 100 of water. The hydrated salt melts at 85°. An aqueous solution of this salt or of sodium phosphate (p. 717) is used for fireproofing draperies, because the crystals deposited in the fabric melt easily, and the fused material protects the fibers from access of oxygen. When heated more strongly alum loses its water of hydration, together with some sulphur trioxide, and leaves a slightly basic, anhydrous salt known as **burnt alum.** A solution of alum dissolves a considerable amount of aluminium hydroxide, giving "neutral alum," a basic salt $K_2SO_4,Al_4(OH)_6(SO_4)_3$ used as a mor-

dant (see p. 648). The substance is usually prepared by adding sodium carbonate to the solution of alum as long as the aluminium hydroxide, formed locally, continues to redissolve. Potash-alum and ammonium-alum are more easily freed from impurities (*e.g.*, compounds of iron) by recrystallization than is aluminium sulphate, and the alums are therefore used instead of the latter in medicine and in dyeing delicate shades. Alum was formerly extensively employed to replace cream of tartar in baking powder (p. 631). In the last case, the reaction:

$$K_2SO_4,Al_2(SO_4)_3,24H_2O + 6NaHCO_3 \rightarrow K_2SO_4 + 3Na_2SO_4 + 2Al(OH)_3 + 6CO_2 + 24H_2O$$

liberates carbon dioxide by hydrolysis of the aluminium carbonate (p. 682).

Ammonium-alum $(NH_4)_2SO_4,Al_2(SO_4)_3,24H_2O$ and **chrome-alum** $K_2SO_4,Cr_2(SO_4)_3,24H_2O$ are the most familiar alums after **potash-alum.** The former is used as a source of aluminium hydroxide, and the latter in the "fixing bath" to harden the gelatine on photographic films and plates.

Aluminium sulphate and alum are also used in the **foam type of fire extinguishers.** Most foam extinguishers resemble the acid-soda type in appearance (see Fig. 164, p. 568). The outer can contains a solution of sodium bicarbonate, but instead of having a bottle of acid suspended from the cover there is a long cylinder filled with a solution of aluminium sulphate or alum. There is also added to the sodium bicarbonate solution a substance which will give a tough foam. Extracts of licorice are usually employed. When this type of extinguisher is inverted the reaction between the sodium bicarbonate and alum gives off carbon dioxide, which mingles with the licorice extract and comes out of the nozzle as a heavy foam consisting of tough-skinned bubbles filled with the gas. This foam clings tenaciously to any fire and quickly smothers it. This type of extinguisher is especially suitable for all types of oil fires.

Water Purification: Coagulation Process. — The suspended matter in water to be used for a domestic supply can be coagulated into larger particles by introducing a small amount of the gelatinous precipitate of aluminium hydroxide. These larger particles, which adsorb also the greater part of the bacteria, settle rapidly and the process therefore permits the use of relatively small settling ponds. Aluminium sulphate, made from crude bauxite, and lime are added to the water:

$$3Ca(OH)_2 + Al_2(SO_4)_3 \rightarrow 3CaSO_4 + 2Al(OH)_3.$$

If the water has much temporary hardness, lime is not required:

$$3Ca(HCO_3)_2 + Al_2(SO_4)_3 \rightarrow 3CaSO_4 + 2Al(HCO_3)_3.$$

The carbonate of aluminium, being a salt of *both* a very weak acid and a very weak base, is extensively hydrolyzed (p. 682):

$$Al(HCO_3)_3 + 3H_2O \rightarrow Al(OH)_3 \downarrow + 3H_2CO_3$$

so that aluminium hydroxide is precipitated.

Crude ferrous sulphate $FeSO_4$ (copperas), being in many places cheaper than aluminium sulphate, is often used instead of the latter. The lime precipitates ferrous hydroxide $Fe(OH)_2$. This is quickly oxidized to the red ferric hydroxide $Fe(OH)_3$, which coagulates the suspended matter.

Clay and Pottery. — By the action of water and carbon dioxide upon granite and other rocks containing feldspar $KAlSi_3O_8$, the potash is slowly removed, and the compound is changed largely into a hydrated orthosilicate $H_2Al_2(SiO_4)_2,H_2O$. When pure, it forms **kaolin** or china clay, a white, crumbly material. When washed away and redeposited, it usually acquires compounds of iron, the carbonates of calcium and magnesium, and sand (silica), becoming common clay. Ocher, umber, and sienna are clays colored with oxides of iron and manganese. Fuller's earth is a purer variety.

The plasticity of clay, a property connected with the colloidal nature of the kaolin, enables it to be fashioned into various shapes. When heated, it shrinks and becomes a hard, solid, porous mass, and does not melt. These two properties enable us to use it in making bricks, pottery, and porcelain. The presence of calcium and magnesium compounds makes the clay more fusible, because it permits the formation of fusible silicates of these metals. **Bricks** and **tiling** for roofs and drains are made of common clay and sand and, when red, owe their color to oxide of iron Fe_2O_3. The firing is done with fuel gas in ovens or kilns of brickwork. To glaze drain pipes and some bricks, salt is thrown into the kiln. The water vapor, at a red heat, hydrolyzes the salt, hydrogen chloride is set free, and the sodium hydroxide gives with the clay a fusible sodium-aluminium silicate which fills the surface pores. Clay for fire-brick (infusible) must contain silica, but no lime.

China and **porcelain** are made from pure clay, free from iron, to which a little of the more fusible feldspar is added. After the first firing, the articles are porous (bisque), and must be covered with a glaze to make them water-tight. A paste of finely-ground

feldspar and silica, sometimes containing lead oxide, is spread on the surface, and the articles are fired again, at a higher temperature. The feldspar melts and fills the pores, so that a continuous, semi-transparent material results. Colored decorations are added by means of suitable materials, mainly oxides of metals which give colored silicates. A third firing causes these oxides to interact and fuse with the glaze. Porcelain, if made with sufficient clay, is very infusible. It is attacked by aqueous and by fused alkalies, however, giving soluble silicates.

The Schwerin process for separating ferric oxide Fe_2O_3 from clay, so that white porcelain may be obtained, is now used on a large scale and affords an interesting application of the properties of colloidal suspensions (p. 642). When the impure clay is suspended in water, the particles of ferric oxide are positively charged and those of the clay are negative. By inserting plates connected with the dynamo in the trough, the clay particles are caused to drift towards the positive plate and the ferric oxide towards the other, so that, when the liquid from the positive end is allowed to settle, pure clay is obtained.

In making bricks, in some cases, advantage is taken of the fact that negative colloids, such as clay, become more strongly negative in presence of a trace of free alkali. Thus, when a trace of sodium hydroxide is added to clay slip, the particles repel one another more strongly, the cohesion which causes the plasticity is reduced, and the clay can be poured into molds. This avoids diluting the clay with water, which would only have to be driven out again, with great waste of heat, in the firing.

Ultramarine. — Pulverized *lapis lazuli,* a rare mineral of beautiful blue color, was used by artists in the past as a pigment. Gmelin (1828) found a way of making it artificially. A mixture of kaolin, sodium carbonate, sulphur, and charcoal is heated until a green mass is obtained. This mass is then pulverized and heated with more sulphur. The product is used as laundry blueing, in making blue-tinted paper, and with oil in making paint. It is also added in small amount to correct the natural faintly yellow tint of linen, starch, sugar, and paper-stock. By varying the mode of heating, without altering the composition, various colors from green to reddish violet can be obtained. No pure colored substance can be extracted from it. The variety of colors is due to different degrees of colloidal dispersion of some substance suspended in the solid (compare p. 649).

Cement. — Portland cement is made by heating a pulverized mixture of a material rich in lime, such as limestone $CaCO_3$, with one in which silica, iron oxide and alumina are the main constitu-

ents, such as common clay. Some natural rocks contain all of the necessary elements in suitable proportions. The finely powdered material is first burnt or raised to a temperature of 1400°–1600°, at which temperature it fuses partially and forms lumps or *clinkers*. The process is made continuous, in industrial practice, by feeding the moistened powder slowly in at the upper end of a slightly inclined revolving cylinder of iron (20 to 45 by 2 meters). The motion continually turns over the thin layer, and exposes every particle to the heat of the air-blast, charged with pulverized coal, burning in the interior. The product slides out in a continuous stream at the lower end, and when it has cooled it is mixed with 2–3 per cent of gypsum and pulverized again. The resulting product is **Portland cement,** the manufacture of which in the United States alone now exceeds 75,000,000 barrels (of 380 pounds) yearly.

Portland cement is essentially a mixture of complex silicates (see p. 663) and aluminates of calcium, containing excess lime. Various views have been advanced regarding the mechanism of the setting reaction when water is added, but the equations originally put forward by Le Chatelier are now generally favored. According to Le Chatelier, the most important components of Portland cement are tricalcium silicate $3CaO,SiO_2$ and tricalcium aluminate $3CaO,Al_2O_3$, which react as follows:

$$2[3CaO,SiO_2] + 9H_2O \rightarrow [2CaSiO_3,5H_2O] + 4Ca(OH)_2$$
$$3CaO,Al_2O_3 + Ca(OH)_2 + 11H_2O \rightarrow 4CaO,Al_2O_3,12H_2O.$$

The rate of the hydration of the various products formed is the main factor determining the rapidity of the setting and hardening of the cement.

The small amount of *gypsum* added also regulates the setting time of the cement. The *iron oxide* is necessary to assist in the burning and to lower the temperature at which the mixture begins to fuse. If too large a quantity of *excess lime* is present, the cement will be unsound and liable to crack on drying. Too little excess lime gives a cement which sets too quickly and is lacking in strength.

Concrete is a mixture of cement with sand and crushed stone or gravel, all made into a paste with water. It sets to a solid mass, suitable for walks, and for the foundations, walls, and floors of buildings. Since no carbon dioxide from the air is required in the hardening process (contrast with p. 728), it sets equally well under water (hence hydraulic cement), and is employed in constructing dams, levees, and the foundations of bridges. Reinforced concrete contains twisted rods of iron, embedded in the mass, and is much used in building construction.

Blast-furnace slag (p. 896), when pulverized and heated with limestone, has been found to yield an excellent quality of cement, and a valuable use has thus been found for what was formerly an annoying encumbrance.

Portland cement is also manufactured now by strongly heating clay with gypsum (p. 728), sulphuric acid from the oxides of sulphur liberated forming an important by-product of the process.

Analytical Reactions of Aluminium Compounds. — The alkalies, and alkaline solutions like that of ammonium sulphide, precipitate the white hydroxide. The product is soluble in excess of the active alkalies. Soluble carbonates also throw down the hydroxide. Aluminium compounds, when heated strongly in the flame with cobalt salts, give a blue aluminate of cobalt $Co(AlO_2)_2$.

Exercises. — 1. What are the differences between zinc and aluminium, and their corresponding compounds?

2. Construct equations showing, (*a*) the hydrolysis of aluminium sulphate (p. 773), (*b*) the interaction of aluminium sulphate and cobalt nitrate in the Bunsen flame.

3. Formulate the ionization of aluminium hydroxide (compare p. 748).

4. Why does zinc hydroxide, in spite of its feebleness as an acid, dissolve in ammonium hydroxide, while aluminium hydroxide does not (see p. 748)?

5. Make equations for the following actions: (*a*) aluminium on hydrochloric acid; (*b*) aluminium on mercuric chloride $HgCl_2$; (*c*) displacement of manganese from manganese dioxide by aluminium.

6. Why is the tarnish on aluminium the oxide, and not the carbonate (as on Zn and Mg)? What qualities in a tarnish enable it to protect the metal from further oxidation (p. 850)?

7. Make equations for the action of bicarbonate of soda on anhydrous sodium aluminium sulphate (p. 632) when heated. Explain what raises the bread.

8. Why does ammonium sulphide precipitate aluminium hydroxide, and not aluminium sulphide, from solutions of soluble aluminium salts?

9. Tabulate the points of resemblance and of difference in the solubility relationships of thallous and silver salts. [Use the table on the inside front cover.]

10. Calculate the atomic weight of scandium from the following data: 2.5988 g. of scandium bromide $ScBr_3$ were found to have a bromine content equivalent to 2.9527 g. of silver.

11. Calculate the atomic weight of dysprosium from the following data: 2.2513 g. of dysprosium chloride $DyCl_3$ were found to have a chlorine content equivalent to 2.7099 g. of silver.

12. What volume of hydrogen at 15° and 750 mm. will be obtained by the action of excess NaOH on 100 g. of aluminium?

13. What will happen if a solution of washing soda is boiled in an aluminium pan? Why?

14. Solutions of aluminium chloride and sodium aluminate are mixed together in equivalent quantities. What do you observe? Formulate ionically.

15. From the following thermochemical equations:

$$4Al + 3O_2 \rightarrow 2Al_2O_3 + 760{,}000 \text{ cals.}$$
$$4Fe + 3O_2 \rightarrow 2Fe_2O_3 + 392{,}000 \text{ cals.}$$

calculate the heat evolved when 1 g. atomic wt. of aluminium powder is ignited to reduce an equivalent amount of Fe_2O_3.

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CHAPTER XLVI

COPPER AND MERCURY

Up to the present we have followed fairly closely, in our order of presentation of the metals, the electromotive series on page 313. If we were to continue on this basis, the next two elements to come up for consideration would be manganese and chromium. The chemical relations of these elements, however, are so complex that it is advisable to postpone their discussion until a later chapter. We shall consequently resume our study of the metals by taking up at this point two elements which will introduce us to these complexities of behavior somewhat more easily — namely copper and mercury.

Although these metals are placed in different columns of the periodic system, they offer many striking resemblances, as will appear in the following sections. Both elements fall below hydrogen in the electromotive series.

The Chemical Relations of the Copper Family. — Copper (Cu, atomic number 29), silver (Ag, at. no. 47), and gold (Au, at. no. 79), occupy the right side in the second column of the table of the periodic system (p. 446), and the chemical relations (p. 680) of these elements are in many ways in sharp contrast to those of the alkali metals, their neighbors, on the left side:

Alkali Metals	Copper, Silver, Gold
Very active; rapidly oxidized by air; displace all other metals from combination (electromotive series, p. 313).	Amongst least active metals; only copper is oxidized by air; displaced by most other metals. Hence, found free in nature (p. 143).
All univalent and give but one series of compounds. Halides all soluble in water.	Cu^{I} and Cu^{II}: two series. Ag^{I}: one series.* Au^{I} and Au^{III}: two series. Halides of univalent series insoluble.
Oxides and hydroxides strongly basic, and halides not hydrolyzed (p. 406).	Oxides and hydroxides feebly basic (except Ag_2O); halides hydrolyzed (except Ag-halides). Hence, basic salts are numerous.
Never found in anion. Give no complex cations.	Frequently in anion, *e.g.*, $K.Cu(CN)_2$, $K.Ag(CN)_2$, $K.AuO_2$, $K.Au(CN)_2$, and in complex cation, *e.g.*, $Ag(NH_3)_2.OH$ and $Cu(NH_3)_4.(OH)_2$.

* A few complex compounds are known in which silver is bivalent.

On account of their inactivity towards oxygen, and their easy recovery from combination by means of heat, silver and gold, together with the platinum family, are known as the "noble metals." Consideration of these elements will be deferred to the following chapter (Chapter XLVII).

Univalent copper and gold resemble in some ways Hg^{I} and Tl^{I}, while bivalent copper resembles Zn^{II}, Mn^{II}, Fe^{II}, and Ni^{II}, and trivalent gold resembles Pt^{IV}. This family is, in fact, not homogeneous, and the close relation which, amongst metals, subsists between valence and chemical properties (see p. 450) makes comparisons with elements of entirely different families often the most suggestive.

COPPER Cu

Chemical Relations of the Element. — Copper is the first metallic element showing two valences which we have encountered. In such cases two more or less complete, independent series of salts are known. These are here distinguished as **cuprous** (univalent) and **cupric** (bivalent) salts. The methods by which a compound of one series may be converted into the corresponding compound of the other series should be noted.

The chief cuprous compounds are Cu_2O, CuCl, CuBr, CuI, CuCN, Cu_2S. The cuprous compound is in each case more stable (p. 173) than the corresponding cupric compound, and is formed from it either by spontaneous decomposition, as in the cases of the iodide and cyanide ($2CuI_2 \rightarrow 2CuI + I_2$), or on heating. The cuprous halides and cyanide are colorless and insoluble in water. Cuprous-ion Cu^+ seems to be colorless. The cuprous salts of the oxygen acids are unstable.

The cupric compounds are more numerous, as they include also stable salts of oxygen acids, like $CuSO_4$, $Cu(NO_3)_2$, etc. CuI_2 and $Cu(CN)_2$ cannot be obtained in pure form, as they decompose, giving the cuprous salts. The anhydrous salts are usually colorless or yellow, and it appears probable that the true cupric-ion Cu^{++} is also colorless.* Hydrated salts of copper, however, are blue in

* Not only is anhydrous copper sulphate itself *colorless*, but it dissolves sparingly in 100 per cent sulphuric acid to give *a colorless solution* which conducts the electric current fairly well, although the anhydrous acid, like most pure liquids, is practically a non-conductor. If such a solution is heated in a partially-filled sealed tube it becomes blue in color, due to the loss of sulphur trioxide from the solvent and the consequent availability of water for the hydration of the cupric ions. As the tube is cooled, the color disappears again.

color, and so are dilute aqueous solutions of copper salts, presumably owing to the blue coloration of "hydrated" cupric-ion $Cu(H_2O)_x^{++}$. It is to be noted that "ammoniated" cupric-ion $Cu(NH_3)_4^{++}$ is colored a still brighter blue (see p. 787). The cupric are more familiar than the cuprous compounds, since cupric oxide, sulphate, and acetate are the compounds of copper which most frequently find employment in chemistry and in the arts. All the soluble salts of copper are **poisonous.**

In addition to (1) **having two valences** Cu^{I} and Cu^{II}, and therefore two series of compounds (*two* oxides, *two* chlorides, etc.), *each* of these states of copper also combines with certain compounds to produce (2) **complex positive ions** such as $Cu(NH_3)_2^+$ and $Cu(NH_3)_4^{++}$, just as hydrogen and ammonia form the complex positive ion NH_4^+, and the univalent form also gives (3) **stable complex negative ions** such as $Cu(CN)_2^-$, $CuCl_2^-$. Only zinc and cadmium, among all of the metallic elements discussed in the preceding chapters, showed any of these peculiarities. Many of the metals to be discussed later exhibit one or more of them, however. **Especial attention should therefore be given to the chemistry of copper,** in order that the behavior which such relations entail may be mastered at the first encounter, and the same relations may be instantly recognized and understood when they reappear in other connections.

In electrolyzing salts of copper, a given amount of electricity will deposit twice as much copper from a cuprous salt as from a cupric salt (p. 346), since cuprous-ion carries only half as great a charge, weight for weight, as cupric-ion.

Writers on chemistry still (p. 152) frequently double the formulæ of cuprous salts (Cu_2Cl_2, etc.). The molecular weights in organic solvents (see p. 215), however, in many cases accord with the simple formulæ. Some higher molecular weights observed in solution, the vapor density of cuprous chloride (6.6, corresponding nearly to Cu_2Cl_2) and the formation of numerous double or complex compounds like HCl,CuCl ($=HCuCl_2$), which may be regarded as acid salts, however, are facts which lend support to the view that the formulæ should be doubled. Inasmuch as the behavior of the salts is sufficiently well represented by the simple empirical formulæ, these are here used throughout.

Occurrence.—Copper is found **free** in considerable amounts, particularly on the Michigan shore of Lake Superior. Other valuable deposits and ores exist in Arizona, Montana and Utah, in the Katanga district of the Belgian Congo, in Chile, in China, and in Japan. A large proportion of commercial copper is obtained from

chalcopyrite, Cu_2S,Fe_2S_3. The sulphides, **copper pyrites** $CuFeS_2$ and **chalcocite** Cu_2S, are worked in Montana, in southwest England, and in Spain. **Malachite,** $Cu_2(OH)_2CO_3$ ($= Cu(OH)_2,CuCO_3$), and **azurite,** $Cu_3(OH)_2(CO_3)_2$ ($= Cu(OH)_2,2CuCO_3$), both basic carbonates, are mined in Arizona, Siberia, and elsewhere. The former is often used as an ornamental stone. **Cuprite** or ruby copper Cu_2O is also an important ore. The name of the element comes from the fact that in ancient times copper mines, long since worked out, existed in Cyprus. The element is found in the feathers of some birds, in the hæmocyanin of the blood of the cuttle-fish, which is blue when arterial and colorless when venous, and elsewhere in living organisms.

Extraction from Ores. — For isolating native copper it is only necessary to separate the metal, by grinding and washing, from the rock through which it ramifies, and to melt the almost pure powder of copper with a flux (p. 683). The carbonate and oxide ores require coal, in addition, for the removal of the oxygen.

The liberation of copper from the sulphide ores is difficult, and often involves very elaborate schemes of treatment. This arises from the fact that many sulphur ores contain a large amount of the sulphides of iron, and these have to be removed by conversion first into oxide (by roasting) and subsequently into silicate (with sand).

Roasting *first* removes much of the sulphur as sulphur dioxide, leaving Cu_2O and Fe_2O_3. *Next* the roasted material is treated in a blast furnace (p. 896), along with "green" (unroasted) ore, sand (if silica is not present in the ore), and coke. Some of the iron is oxidized and removed in the slag (as silicate). The product, known as copper "matte," is a mixture of cuprous sulphide Cu_2S with ferrous sulphide FeS. The *third* stage is to bessemerize (see p. 899) the melted matte with sand in a converter. Here the rest of the iron is oxidized and eliminated as silicate in the slag, and the sulphur escapes as SO_2. The slag and metallic copper are poured separately. The latter gives off some dissolved sulphur dioxide in bubbles as it solidifies and, from its appearance, is named **blister copper.** *Finally,* since the copper now contains dissolved cuprous oxide Cu_2O, the blister copper is melted and "poled," by stirring with green wood. The gases (hydrocarbons, etc., p. 622) given off by the heated wood reduce the oxide to copper. If the copper is to be refined electrolytically (p. 794), it is then cast in plates 3 feet square and ¾ inch thick.

Much copper ore is of low grade, containing perhaps only 2 per cent of copper ore and 98 per cent of rock material. The old methods of concentrating copper sulphide ores by simple washing left large amounts of copper in the rejected gangue. Recent **flotation processes** prevent this loss. The ore is finely ground and beaten up with water containing a small quantity of oil. The particles of copper sulphide become wetted by the oil, the particles of gangue are preferentially wetted by the water. When air is forced through the pulp, the copper sulphide particles float with the froth to the top and are scraped off, while the gangue sinks to the bottom Sixty million tons of poor grade ore per year are now treated by this method, and enormous stacks of rejected tailings have been successfully re-worked.

Physical Properties. — Copper is red by reflected and greenish by transmitted light. Native copper shows crystals of the regular system (p. 67). It melts at 1083°, and therefore much more easily than pure iron (1535°). Its density is 8.93. When steel draw-plates are used, it can be drawn into wire with a diameter of only 0.2 mm., and by means of plates provided with perforated diamonds the diameter of the wire can be reduced to 0.03 mm. (1 kilometer weighs only 7 g). The metal after drawing is more tenacious, but conducts electricity less well.

Chemical Properties. — In dry oxygen, copper does not rust. In moist oxygen a thin film of cuprous oxide is formed, and in ordinary air a green basic carbonate (*not* verdigris, p. 792). It does not decompose water at any temperature or displace hydrogen from dilute acids (p. 142). On the other hand, hydrogen, adsorbed on platinum (compare p. 534) or even on charcoal, liberates copper: $Cu^{++} + H_2 \rightarrow Cu + 2H^+$, when immersed in solutions of copper salts. The metal attacks oxygen acids (pp. 415, 532), however. Again, acids like hydrochloric acid, in conjunction with oxygen from the air, do act slowly upon copper: $2Cu + 4HCl + O_2 \rightarrow 2CuCl_2 + 2H_2O$. This sort of simultaneous action of two agents is frequently used, as in making silicon tetrachloride (p. 659). In a similar way sea-water and air slowly corrode the copper sheathings of ships, giving a basic chloride, $Cu_4(OH)_6Cl_2,H_2O$ ($= 3Cu(OH)_2,CuCl_2,H_2O$), which is found in nature as **atakamite.**

On account of its resistance to the action of acids, copper is used for kettles, stills and evaporating pans, for covering roofs and ships' bottoms, and for coins. It furnishes also electrotype reproductions of medals, of engraved plates, of type, etc. (see p. 793). Great quantities of the metal are used for electrical wires and cables. Traces of other metals greatly reduce the conductivity. Thus arsenic

amounting to 0.03 per cent lowers the conductivity about 14 per cent (see also p. 694).

The total world's production of copper in 1935 was 1,650,000 tons, of which 381,000 tons were from the United States.

Alloys. — The qualities of copper are modified for special purposes by alloying it with other metals. **Brass** contains 18–40 per cent of zinc, and melts at a lower temperature (p. 693) than does copper. A variety with little zinc is beaten into thin sheets, giving Dutch metal ("gold leaf"). **Bronze** contains 3–8 per cent of tin, 11 or more per cent of zinc, and some lead. It was used for making weapons and tools before means of hardening iron were known, and later, on account of its fusibility, continued to be employed for castings until displaced largely by cast-iron (discovered in the eighteenth century). For works of art it is preferred to copper because of its fusibility, its color, and its more rapid acquirement of a much prized "patina," due to surface corrosion. Artificial "bronzing" of brass is affected by applying a solution of arsenious oxide in hydrochloric acid ($AsCl_3$). The zinc displaces some arsenic, which combines with the copper. Brass instruments are "bronzed" by means of a dilute solution of chloroplatinic acid (p. 817), from which the zinc displaces platinum. **Gun-metal** contains 10 per cent, and **bell-metal** 20–24 per cent of tin. **German silver** contains 19–44 per cent of zinc and 6–22 per cent of nickel, and shows none of the color of copper. **Aluminium-bronze** contains 5–10 per cent of aluminium, and resembles gold in color. When it contains some iron, it can be worked at a red heat, but not welded. **Silicon-bronze** contains not more than 5 per cent of silicon, and is made by adding silicide of copper (produced in the electric furnace, p. 563) to copper. It has about only 60 per cent of the conductivity of pure copper, but is nearly twice as tenacious, and is used for telephone and over-head electric wires. **Phosphor-bronze** contains copper and tin (100 : 9) with ½–1 part of phosphorus, and is employed for certain parts of machines. Ships' propellers are made of **manganese-bronze** (30 per cent manganese). In many of these alloys the metals are partly in the form of chemical compounds, such as Cu_3Sn and Cu_2Zn_3.

Cupric Chloride $CuCl_2$. — This compound is made by union of copper and chlorine, or by treating the hydrate or carbonate with hydrochloric acid. The blue crystals of **a hydrate,** $CuCl_2,2H_2O$, are deposited by the solution. The **anhydrous salt** is yellow. Dilute solutions are blue, the color of hydrated cupric-ion, but concen-

trated solutions are green, presumably on account of the presence of complex ions $CuCl_4^{=}$. The aqueous solution is acid in reaction (p. 408). When excess of ammonium hydroxide is added to the solution, the basic chloride, which is at first precipitated, redissolves, and a deep-blue solution is obtained (see p. 789). This on evaporation yields deep-blue crystals of hydrated **ammonio-cupric chloride** $Cu(NH_3)_4Cl_2,H_2O$. The deep-blue color of the solution, which is given by all soluble cupric salts on addition of ammonia in excess, is that of ammonio-cupric-ion $Cu(NH_3)_4^{++}$. The dry salt also absorbs ammonia, giving $CuCl_2,6NH_3$. Such compounds of ammonia with salts are extremely common, and are exactly analogous to hydrates. On reducing the partial pressure of ammonia above the salt, the compound is dissociated (compare p. 689).

Cuprous Chloride CuCl. — This salt may be made by boiling cupric chloride solution with hydrochloric acid and copper turnings:

$$CuCl_2 + Cu \rightarrow 2CuCl, \text{ or } Cu^{++} + Cu \rightarrow 2Cu^{+}.$$

Soluble compounds of cuprous chloride with hydrogen chloride (*e.g.*, $HCuCl_2$, see p. 783), are formed, which are decomposed when the acid solution is diluted with water. Cuprous chloride itself is insoluble in water, and forms a white crystalline precipitate.

Cuprous chloride is hydrolyzed quickly by *hot* water, giving, finally, red, hydrated cuprous oxide, Cu_2O. Its solution in hydrochloric acid is oxidized by the air, turning first brown and then green, and finally depositing cupric oxychloride. It also has the power of absorbing carbon monoxide, to form a compound said to be $Cu(CO)Cl,H_2O$, and this property is used to separate this gas in analyzing mixtures of gases. Cuprous chloride also dissolves (see p. 788) in ammonium hydroxide, giving **ammonio-cuprous chloride** $Cu(NH_3)_2Cl$, the ion $Cu(NH_3)_2^{+}$ being colorless. The solution is quickly oxidized by the air, turns deep-blue, and then contains $Cu(NH_3)_4^{++}$.

The Bromides and Iodides of Copper. — By treatment of copper with bromine-water, and slow evaporation of the solution, jet-black crystals of anhydrous **cupric bromide** $CuBr_2$ are obtained. A concentrated solution of this salt in water is dark-brown, but on dilution the color changes first to green and finally to blue. This is ascribed to the progressive dissocation of the complex ion $CuBr_4^{=}$ (deep brown) into hydrated Cu^{++} (blue) and Br^{-} (colorless) on

addition of water. When dry cupric bromide is heated, bromine **is** given off, and **cuprous bromide** CuBr remains.

Cupric iodide CuI_2 appears to be unstable at ordinary temperatures. When a soluble iodide is added to a cupric salt, a white precipitate of **cuprous iodide** CuI and free iodine are obtained:

$$2Cu^{++} + 4I^- \leftrightarrows 2CuI\downarrow + I_2.$$

The Solution of Insoluble Salts When Complex Ions Are Formed. — The solution of an insoluble salt like cuprous chloride by hydrochloric acid or ammonium hydroxide is typical of a great variety of actions in which compound or complex ions are concerned. The explanation involves only principles already used in the previous discussion of ionic equilibria (pp. 760–3), and the student may find it advisable at this point to refresh his memory regarding these principles by re-reading the above pages very carefully.

The dissolving of cuprous chloride in ammonium hydroxide to form soluble ammonio-cuprous chloride $Cu(NH_3)_2Cl$ will be considered in some detail as a typical case.

The **solubility product** of cuprous chloride in water is small; in other words, we cannot have a high concentration of Cu^+ ions and a high concentration of Cl^- ions simultaneously in the solution:

$$\downarrow CuCl\ (solid) \rightleftarrows Cu^+ + Cl^-. \qquad (1)$$

But when we add ammonium hydroxide (which is largely free ammonia NH_3, see p. 514) to a solution containing the very low amount of Cu^+ and Cl^- requisite to be in equilibrium with solid CuCl, the ammonia combines with the Cu^+ to form **complex ions** of the type $[Cu(NH_3)_2]^+$. The dissociation of these ions into Cu^+ and $2NH_3$ in the solution is exceedingly slight:

$$Cu^+ + 2NH_3 \rightleftarrows [Cu(NH_3)_2]^+. \qquad (2)$$

Hence the addition of ammonium hydroxide annihilates practically all of the Cu^+ ions in the solution. This disturbs the equilibrium represented in equation (1) above. To replace Cu^+, more CuCl must go into solution, and the process will continue, if enough ammonia is added, until all CuCl present has been dissolved.

The same exact laws of equilibrium used in discussing the dissolving of salts by acids (pp. 761–3) may be applied to the whole procedure. The principles involved are, as we shall find, very ex-

tensively used in analysis (p. 919) and in industrial processes (see p. 812).

The dissolving of cuprous chloride by hydrochloric acid is explained in the same way. The only difference is that here the copper is in complex *negative* ions such as $CuCl_2^-$. The dissociation of these ions into Cu^+ and $2Cl^-$ is also extremely slight:

$$CuCl_2^- \rightleftarrows Cu^+ + 2Cl^-.$$

Consequently a solution in contact with solid CuCl, to which hydrochloric acid is added, loses almost all of its Cu^+ ions, and the salt necessarily dissolves in spite of its small solubility product.

It must be noted very attentively that the dissolving of an insoluble salt by the formation of a complex ion depends upon two factors: (1) **the degree of insolubility of the salt,** and (2) **the stability of the complex ion.** The more insoluble the salt under consideration is, the more complete must be the removal of one of the simple ions of this salt, by formation of a complex ion, for solution to occur. For as soon as the degree of dissociation of the complex ion is sufficient to give a concentration of the simple ion high enough to enable the solubility product of the salt to be reached, it is impossible for more of the salt to pass into solution.

The dissolving of insoluble cupric salts by ammonium hydroxide, already referred to on p. 787, is a good illustration of this point. The deep-blue ion $[Cu(NH_3)_4]^{++}$ is very little dissociated in solution:

$$[Cu(NH_3)_4]^{++} \rightleftarrows Cu^{++} + 4NH_3.$$

Addition of ammonium hydroxide to precipitates of cupric salts results therefore in their complete solution, save only in the case of *cupric sulphide*. This is, as we have already had occasion to mention (p. 763), an *exceptionally insoluble salt*. Even the extremely small concentration of Cu^{++} in the solution which results from the slight instability of the complex ammonio-cupric ion suffices, therefore, *after the merest trace of CuS has been dissolved,* to bring the product of the concentrations of Cu^{++} and $S^=$ in the solution up to the solubility product of copper sulphide, and any further advance of the action is thereby prohibited.

Cupric Sulphate $CuSO_4$. — This, the most familiar salt of copper, is obtained by heating copper in a furnace with sulphur, and admitting air to oxidize the cuprous sulphide. The mixture of cupric sulphate and cupric oxide which is formed is treated with sulphuric acid. The salt is also made by allowing warm dilute sulphuric acid to trickle over granulated copper, while air has free access to the material:

$$2Cu + 2H_2SO_4 + O_2 \rightarrow 2CuSO_4 + 2H_2O.$$

When concentrated and very hot, sulphuric acid will itself act as the oxidizing agent (see p. 415).

Cupric sulphate crystallizes as **pentahydrate** $CuSO_4,5H_2O$ in blue asymmetric crystals (Fig. 27, p. 61), and in this form is called **blue-stone** or **blue vitriol.** The dissociation of this hydrate as the vapor pressure of water above it is reduced has been discussed on p. 689. The aqueous solution has an acid reaction (p. 408). The anhydrous salt is white, and can be crystallized in thin needles from solution in hot, concentrated sulphuric acid (compare p. 888). Cupric sulphate is employed in copper-plating (see p. 793), in batteries, and as a mordant in dyeing. A minute proportion is added to drinking water, to destroy *algæ*, which otherwise propagate in the reservoirs and give a disagreeable taste and odor to the water. The seeds of cereals are moistened with a dilute solution, before planting, to prevent the growth of fungi (smuts).

When ammonium hydroxide is added to cupric sulphate solution, a pale-green basic sulphate is first precipitated. With excess of the hydroxide, the blue $Cu(NH_3)_4{}^{++}$ ion (p. 787) is formed, and crystals of **ammonio-cupric sulphate** $Cu(NH_3)_4.SO_4,H_2O$ can be obtained from the solution.

Cupric sulphate also combines with potassium and ammonium sulphates, giving **double salts** of the form $CuSO_4,K_2SO_4,6H_2O$, which are deposited in large, monosymmetric crystals from the mixed solutions. Double salts (p. 291) exist as such in the solid form only and, in water, are resolved into the components and their ions.

Cupric Hydroxide $Cu(OH)_2$. — The hydroxide is a *blue*, gelatinous *precipitate*, formed by addition of sodium or potassium hydroxide to a solution of a cupric salt: $Cu^{++} + 2OH^- \rightarrow Cu(OH)_2$. When the mixture is boiled, the hydroxide loses water and forms a black, hydrated cupric oxide $Cu(OH)_2,2CuO$ (?). The hydroxide is used as a mordant. A mixture of cupric sulphate solution and milk of lime ($Ca(OH)_2$), — **Bordeaux mixture** — containing cupric hydroxide as a precipitate, is used extensively as a spray on grape vines and other plants, to prevent the growth of fungi.

Cupric hydroxide *dissolves* in ammonium hydroxide solution, forming the soluble compound $Cu(NH_3)_4.(OH)_2$, which has a deep blue color. This ammoniacal solution of cupric hydroxide is employed as a solvent for cellulose in the manufacture of artificial silk (see p. 600). Cupric hydroxide *dissolves* also in an alkaline solution of sodium-potassium tartrate $NaKC_4H_4O_6$ (p. 632), giving

Fehling's solution, a reagent used in testing for glucose and similar reducing agents. When this reagent is added to a liquid containing glucose (p. 602), red cuprous oxide Cu_2O is precipitated.

In Fehling's solution, copper enters into the negative ion, as is shown by electrolysis, interacting apparently with the hydroxyl groups of the tartrate-ion.

Cuprous Oxide Cu_2O. — This oxide, mixed with CuO, is formed by gentle heating of copper in air, and is best prepared by use of Fehling's solution. It is red in color, and is employed in making ruby glass and in coloring porcelain.

The simple **hydroxide** CuOH is unknown, but the precipitate from Fehling's solution, when first formed, has approximately the composition $4Cu_2O,H_2O$, and yields the pure oxide Cu_2O only when heated.

Cuprous oxide is acted upon by hydrochloric acid, giving cuprous chloride, or rather $HCuCl_2$. It also dissolves in ammonium hydroxide, giving, probably, $Cu(NH_3)_2.OH$, which is colorless. With dilute oxygen acids part of it is oxidized, giving the cupric salt, and part is reduced to metallic copper:

$$Cu_2O + H_2SO_4 \rightarrow CuSO_4 + Cu + H_2O.$$

Cupric Oxide. — **Cupric oxide** CuO (black) is formed by heating copper in a stream of oxygen, or by igniting the nitrate, carbonate, or hydroxide. Although not soluble in water, it adsorbs moisture from the air, probably because it is porous and has much surface. When heated strongly it loses some oxygen, and is partly reduced to cuprous oxide.

This oxide is used in the laboratory to ascertain the compositions (and formulæ) of organic compounds (**determination of carbon and hydrogen**). A weighed amount of the organic compound is placed in a horizontal tube, between heated masses of the oxide. A stream of oxygen or air carries the vapor of the organic compound over the cupric oxide, which oxidizes it to water and carbon dioxide. The first is absorbed in a weighed **U**-tube filled with calcium chloride, and the second is caught in a weighed vessel containing potassium hydroxide. From the increase in weight in each case, the corresponding weights of hydrogen and carbon (derived from the weighed portion of the organic compound) are calculated.

Cupric Nitrate $Cu(NO_3)_2,6H_2O$. — The nitrate is made by treating cupric oxide or copper with nitric acid (p. 532), and is ob-

tained from the solution as a deliquescent, crystalline **hexahydrate.** When dehydrated at 65° the salt is partly hydrolyzed, and a basic nitrate $Cu_4(OH)_6(NO_3)_2$ remains.

Carbonate of Copper. — No normal carbonate ($CuCO_3$) can be obtained. A **basic carbonate** (malachite) is found in nature, and is precipitated by adding soluble carbonates to cupric salts:

$$2CuSO_4 + 2Na_2CO_3 + H_2O \rightarrow Cu_2(OH)_2CO_3 + 2Na_2SO_4 + CO_2.$$

The carbonate, if formed, would be hydrolyzed by water (p. 682).

Cyanides of Copper. — With potassium cyanide and a solution of a cupric salt, **cupric cyanide** $Cu(CN)_2$ is precipitated. This is not stable, however, and gives off cyanogen, leaving **cuprous cyanide** CuCN:

$$2Cu(CN)_2 \rightarrow 2CuCN + C_2N_2.$$

Cuprous cyanide is insoluble in water, but interacts with an excess of potassium cyanide solution, producing a colorless liquid, from which $K.Cu(CN)_2$, **potassium cuprocyanide,** may be obtained in colorless crystals. The complex anion $Cu(CN)_2^-$ is so little dissociated to Cu^+ and $2CN^-$ that all insoluble copper compounds, *including cupric sulphide*, are dissolved by potassium cyanide; and none of them can be precipitated from the solution. Zinc is actually unable to displace copper from such a solution (see pp. 851–2).

Cupric Acetate. — By the oxidation of plates of copper, separated by cloths saturated with acetic acid (vinegar), a basic acetate of copper (**verdigris**) is obtained:

$$6Cu + 8HC_2H_3O_2 + 3O_2 \rightarrow 2Cu_3(OH)_2(C_2H_3O_2)_4 + 2H_2O.$$

It is used in manufacturing green paint, is insoluble in water, and is unaffected by light. It dissolves in acetic acid, and green crystals of the **normal acetate** $Cu(C_2H_3O_2)_2,H_2O$ are obtained from the solution. The basic acetate is used in preparing **Paris green.** A hot solution of arsenious acid H_3AsO_3 is mixed with a paste of verdigris and a little acetic acid and boiled. A precipitate of Paris green $Cu(C_2H_3O_2)_2,Cu_3(AsO_3)_2$, which has a unique light-green color, is thrown down. On account of their poisonous nature, this compound and **Scheele's green** $CuHAsO_3$ are now little used as pigments. The former is chiefly made for use in the extermination of potato-beetles and other insects and for employment in the destruction of parasitic fungi.

Analytical Reactions of Compounds of Copper. — The ion of ordinary solutions of cupric salts, cupric-ion Cu^{++}, is blue, and that of cuprous salts, cuprous-ion Cu^{+}, is colorless. Cuprous solutions, however, are easily oxidized by the air and become blue. In solutions containing cupric-ion, hydrogen sulphide precipitates black cupric sulphide, even in presence of acids (p. 763). Bases throw down the blue hydroxide, and carbonates precipitate a green basic salt (p. 792). Potassium ferrocyanide gives the brown, gelatinous **cupric ferrocyanide:**

$$2CuSO_4 + K_4.Fe(CN)_6 \rightleftarrows Cu_2.Fe(CN)_6 \downarrow + 2K_2SO_4.$$

A characteristic test is the formation of the deep-blue $Cu(NH_3)_4^{++}$ ion with excess of ammonium hydroxide. This solution itself responds to certain precipitants only (*e.g.*, H_2S). Solutions of complex cuprous cyanides such as $KCu(CN)_2$ are colorless, and do not respond to any of the above tests. With microcosmic salt or borax (pp. 553, 668), copper compounds form a bead which is blue in the oxidizing part of the flame and becomes red and opaque (liberation of copper) in the reducing flame.

More active metals, such as zinc or iron, displace copper from solutions of its salts, so that a blade of a knife, for example, receives instantly a red coating of copper when immersed in such a solution:

$$Fe + Cu^{++} \rightarrow Fe^{++} + Cu \downarrow .$$

Copper Plating. — When platinum or carbon plates, connected with a battery, are immersed in a solution of cupric sulphate, copper is deposited on the negative plate (cathode). The $SO_4^{=}$ migrates towards the positive plate (anode) and there oxygen is liberated and sulphuric acid accumulates around the electrode, which is itself unchanged (see p. 308).

If the anode is made of copper itself, however, copper goes into solution from the anode (Fig. 207) as Cu^{++}, in amount equal to that deposited on the other plate. Thus the quantity of cupric sulphate in solution remains unchanged, and the effect is, virtually, to transfer copper from the copper anode to the cathode.

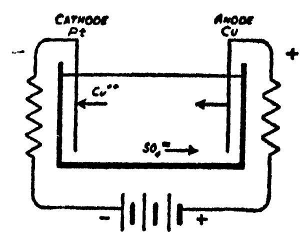


FIG. 207. Electrolysis of Copper Sulphate.

Electrotypes. — A copper electrotype of an object like a medal is made by first preparing a cast of the medal in plaster of Paris or wax. The surface

of this is rubbed with graphite, to render it a conductor, and the cast is used as the cathode in a cell like that just described. The deposit of copper, when stripped off, is found to show an exact reproduction of the engraving, etc., on the object.

Book plates are made by taking a cast of each page of type, preparing the copper electrotypes, and then strengthening and thickening it by filling the back with melted lead. The printing is then done from the electrotype. For newspapers this process is too slow, and the plate is made from the cast by means of melted stereotype metal (lead, antimony, tin; 82 : 15 : 3).

Copper Refining. — The copper, as obtained from its ores by the treatment already described (p. 784), contains a certain amount of silver, gold, and baser metals. The former pay for the cost of refining, and the simultaneous removal of the latter gives pure copper suitable for electrical purposes.

The principle of the electrolytic method of purification employed is the same as that used in electroplating. The heavy plates of poled copper (p. 784) are hung at intervals in large, lead-lined vats of copper sulphate solution and form the anodes (Fig. 208, diagrammatic, view from above). The cathodes consist of thin sheets of copper, which are coated with graphite to permit the metal deposited on them, when the current is passed through the solution, to be easily stripped off. These sheets hang in the vat between the anodes. As the electrolysis proceeds, the copper from the anodes, along with such traces of more active metals, like zinc, as are present as impurities therein, is ionized and goes into solution, until the anode is reduced to a skeleton and is exchanged for a fresh one. The less active metals, such as silver and gold, as well as traces of sulphides, are not ionized. They fall to the bottom of the vat, as a sort of dense mud. At the cathodes, copper ions alone are discharged and deposited, because copper is the least active of the metals present in ionic form. In this way copper, 99.8 per cent pure, can be obtained, and gold and silver are recovered from the mud. The bath liquid is removed from time to time for purification from the more active metals which accumulate in it.

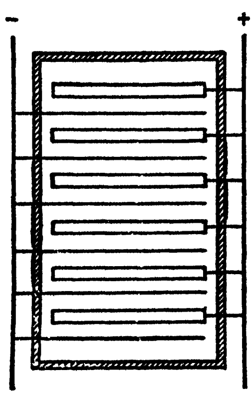


FIG. 208. Copper Refining.

Mercury Hg

Chemical Relations of the Element.* — Like copper, **mercury** (Hg, atomic number 80) enters into **two series** of compounds, the **mercurous** Hg^{I} and the **mercuric** Hg^{II}. The mercurous halides, like the cuprous halides, are insoluble in water and are decomposed by light. There are, however, stable mercurous as well as mercuric salts of oxygen acids. Both of the oxides, Hg_2O and HgO, are basic exclusively, but in a feeble degree. The hydroxides, like silver hydroxide (p. 808), are not stable, and lose water, giving the oxides. The salts of both sets are markedly hydrolyzed by water, and basic salts are therefore common. Mercury enters into the anions of a number of complex salts, such as $HgCl_4^{=}$, $HgI_4^{=}$, $Hg(CN)_4^{=}$, etc. It does not give complex cations with ammonia resembling those of cadmium, copper, and silver ($Cd(NH_3)_4^{++}$, etc.), from which ammonia is removed by heating, but instead forms a class of ammono-basic mercury compounds like $Hg^{II}NH_2Cl$, all of which are insoluble. The mercuric halides and cyanide show many peculiarities due to their being very little ionized.

The mercury salts of volatile acids, like the corresponding salts of ammonium (p. 514), can all be volatilized completely. Mercury vapor and mercury compounds are **poisonous**, the soluble ones more markedly so than the insoluble ones.

The mercurous salts, as a rule, are formed when excess of mercury is employed, and mercuric salts when excess of the oxidizing acid or other substance is present. Reducing agents convert mercuric into mercurous salts, and oxidizing agents do just the reverse. Mercurous-ion appears to exist in solution in the associated form Hg_2^{++}, rather than as simple Hg^{+}.

As in the case of the cuprous compounds, it is a question whether simple or multiple formulæ, HgCl or Hg_2Cl_2, etc., should be employed for mercurous salts. Pending the discovery of some basis for a decision, the simple formulæ are used here.

Occurrence and Isolation of the Metal. — Mercury occurs **native,** and to a larger extent as red, crystalline **cinnabar**, mercuric sulphide HgS. The chief mines are in Spain, Italy, and California. The metal is sold in iron flasks, containing 76 pounds. The world's production averages 80,000 flasks a year.

The liberation of the metal from its ore is easy, because, when roasted, the sulphide is decomposed, and the sulphur forms sulphur dioxide. The mercury does not unite with the oxygen, for the oxide also is decomposed (p. 23) when strongly heated:

$$HgS + O_2 \rightarrow Hg + SO_2.$$

* See also p. 740.

The vapor of the metal is condensed in long, tortuous flues, and the liquid filtered through chamois-skin. For separation from metallic impurities, like zinc, arsenic, and tin, which are dissolved, it must be distilled.

In the laboratory, where mercury finds many applications, it becomes impure with use, and then adheres to glass, and does not run freely in spherical droplets. For purification it is placed along with a little diluted nitric acid in a separatory funnel (Fig. 84, p. 200), and kept in continual agitation by means of a current of air drawn or blown through the mass. By this treatment, foreign metals, such as sodium or zinc, nearly all of which are much more active than mercury (see p. 142), are converted into nitrates. Pure, dry mercury can be drawn off, when needed, at the bottom. If a high degree of purity is required, the product must be distilled *in vacuo*.

Physical Properties. — Mercury or quicksilver (Latin *hydrargyrum*, from Greek ὕδωρ, water, and ἄργυρος, silver) is a silver-white liquid. At —38.9° it freezes, and at 357° it boils. At ordinary temperatures it has a very small vapor tension, at 15° 0.0008 mm., and at 100° 0.28 mm. The vapor is colorless, does not conduct electricity, and is monatomic. A gold-leaf suspended over mercury becomes amalgamated, since the solution of gold in mercury has a vapor tension smaller than that of pure mercury (p. 212).

On account of its high density (13.6, at 0°) and low vapor tension, the metal is employed for filling barometers and manometers. Its uniform expansion favors its use in thermometers. The tendency to form amalgams, which it exhibits towards all the familiar metals with the exception of iron and platinum (both, however, are "wet" by it), is taken advantage of in various ways. Sodium amalgam, which is solid when the sodium exceeds 2 per cent, and consists mainly of $NaHg_2$, behaves like free sodium, but with moderated activity. A layer of mercury on the zinc plates of batteries reduces the action of the acid on the zinc, while the cells are not in use. Mixtures of mercury with powdered tin, silver, and gold quickly form solid amalgams, and are used by dentists. The employment of mercury in the extraction of gold will be described later (p. 812). Engines have recently been devised, in which mercury vapor replaces the steam of the ordinary boiler. The higher boiling point of mercury, as compared with water, makes a great increase in efficiency theoretically possible.

Chemical Properties. — When kept at a temperature near to its boiling-point, mercury combines slowly with oxygen. Its inactivity towards oxygen when cold places it next to the noble metals. On

account of its general inactivity, it is used in the laboratory for confining gases. It does interact with hydrogen sulphide and hydrogen iodide, however (compare Silver, p. 806). Mercury does not displace hydrogen from dilute acids (p. 142), but with oxidizing acids like nitric acid and hot concentrated sulphuric acid, the nitrates and sulphates are formed.

When triturated, so that it is divided into minute droplets with relatively large surface, mercury is used in medicine (blue pills), and shows an activity which is entirely wanting in larger masses.

Mercurous Chloride HgCl. — This salt (**calomel**) is obtained as a white powder by precipitation from solutions of mercurous salts. It is manufactured by subliming mercuric chloride with mercury:

$$HgCl_2 + Hg \rightleftarrows 2HgCl,$$

or more usually by subliming a mixture of mercuric sulphate, made as described above, with mercury and common salt. It is deposited on the cool part of the vessel as a fibrous crystalline mass. It is slowly affected by light just as is silver chloride. Here, however, the chlorine which is released combines with another molecule of the salt to form mercuric chloride. Since the vapor pressure of calomel reaches 760 mm. before the temperature has risen to the melting-point, the compound sublimes at atmospheric pressure without melting. Its vapor density corresponds to the formula HgCl, but the vapor was shown by Smith and Menzies to consist wholly of $Hg + HgCl_2$. The completeness of the dissociation was ascertained by measuring the partial pressures of the mercury and mercuric chloride in the vapor, and finding that together they equalled the total dissociation pressure. The action is reversed when the temperature falls (compare Ammonium chloride, p. 514). The substance is used in medicine on account of its tendency to stimulate all organs producing secretions.

Mercuric Chloride $HgCl_2$. — By direct union with chlorine the mercuric salt, **corrosive sublimate** $HgCl_2$, is formed. It is usually manufactured by subliming mercuric sulphate with common salt, and crystallizes in white, rhombic prisms. It melts at 277° and boils at 307°. The solubility at 20° is 7.4 parts in 100 of water. The aqueous solution is slightly acid in reaction. The salt is easily reduced to mercurous chloride. When excess of stannous chloride is

added to the solution, the white precipitate of calomel, first formed, passes into a heavy gray precipitate of finely divided mercury:

$$2HgCl_2 + SnCl_2 \rightarrow SnCl_4 + 2HgCl,$$
$$2HgCl + SnCl_2 \rightarrow SnCl_4 + 2Hg.$$

The halides of mercury are very little ionized in solution, the bromide and iodide even less so than the chloride. There is a tendency also to the formation of complex salts, so that the addition of sodium chloride increases the solubility in water, $NaHgCl_3$ being formed. The complex salts, like $K.HgCl_3,H_2O$, $K_2.HgCl_4,7H_2O$, and $NH_4.HgCl_3,H_2O$, are easily made by crystallization from solution. The anions are relatively highly dissociated, however, and the behavior is intermediate between that of complex salts and double salts (p. 687).

Corrosive sublimate, when taken internally, causes death. The variable meaning of the word "poisonous" is well illustrated in this case. The mercuric chloride does not act as a direct poison. It causes changes in the cells of the kidneys so that, after about two weeks, the waste products from the system (urea, etc.) can no longer be eliminated, and death occurs from a sort of auto-intoxication. A very dilute solution is used in surgery to destroy lower organisms and thus prevent infection of wounds. The pharmaceutical tabloids of mercuric chloride contain sodium chloride, because, although the latter diminishes the activity of the compound, it also does away with the formation of insoluble, basic chlorides and hastens solution. Mercuric chloride acts also as a preservative of zoölogical materials, forming insoluble compounds with proteins, and preventing their decay. For the same reason, albumen (white of an egg, a mixture of proteins) is given as an antidote in cases of sublimate poisoning.

The Iodides of Mercury. — **Mercurous iodide** HgI is formed by rubbing iodine with excess of mercury. It also appears as a greenish-yellow precipitate when potassium iodide is added to a solution of a mercurous salt. The compound decomposes spontaneously into mercury and mercuric iodide. The decomposition is much hastened by the use of excess of potassium iodide, which combines with and removes the mercuric iodide (see below):

$$2HgI \rightleftarrows Hg + HgI_2.$$

Mercuric iodide HgI_2 is obtained by direct union of mercury with excess of iodine, or by addition of potassium iodide to a solution of a mercuric salt. It is a scarlet powder, insoluble in water, but sol-

uble in alcohol and ether. It interacts with excess of potassium iodide, forming the soluble, colorless **potassium mercuri-iodide** $K_2.HgI_4$ with which many precipitants fail to give the characteristic tests for mercury compounds (compare p. 793). When heated above 128° the red mercuric iodide turns into a yellow modification, and at 259° this new form melts. On being cooled, the liquid freezes first in the tetragonal yellow form, and below 128°, especially if touched with a glass rod, it changes into the red, monoclinic variety with evolution of heat. Sulphur (p. 400) and ammonium nitrate (p. 708) show similar transition points. When the vapor of the compound is cooled, it first forms thin scales of the yellow form, which is the unstable one at low temperatures, and these turn red when touched. Similarly, precipitation gives first the yellow variety, which presently becomes red (see Transformation by steps, p. 544).

The Oxides. — When bases (excepting ammonium hydroxide, see p. 801) are added to solutions of mercurous salts, the brownish-black **mercurous oxide** Hg_2O is thrown down. Under the influence of light or gentle heat (100°), this compound resolves itself into mercuric oxide and mercury.

Mercuric oxide HgO is formed as a red, crystalline powder, when mercury is heated in air near to 357°, but is usually made by decomposing the nitrate. It is obtained also as a yellow powder by adding bases (excepting ammonium hydroxide, see p. 801) to solutions of mercuric salts.

It was long a matter of contention among chemists whether the difference in activity between the red and yellow forms is due solely to the finer state of division of the latter, or whether the substance is existent in two distinct allotropic varieties. The results of X-ray analysis have recently settled the question by showing the crystal structure of the two forms to be *identical.*

Other Salts of Mercury. — **Mercurous nitrate** $HgNO_3,H_2O$ is formed by the action of cold, diluted nitric acid upon *excess* of mercury. It is hydrolyzed, slowly by cold, and rapidly by warm water, giving an insoluble basic nitrate:

$$2HgNO_3 + H_2O \rightleftharpoons HNO_3 + Hg_2(OH)NO_3 \downarrow.$$

On this account a clear solution can be made only when some nitric acid is added. Free mercury is also kept in the solution to reduce mercuric nitrate, which is formed by atmospheric oxidation:

$$Hg(NO_3)_2 + Hg \rightarrow 2HgNO_3, \text{ or } Hg^{++} + Hg \rightarrow 2Hg^{+}.$$

Mercuric nitrate $Hg(NO_3)_2,8H_2O$ is produced by using excess of warm, concentrated nitric acid with mercury. The aqueous solution is strongly acid, and deposits a yellowish, crystalline, basic nitrate $Hg_3(OH)_2O(NO_3)_2$. The hydrolysis is reversed by adding nitric acid.

Mercurous sulphide Hg_2S is formed by precipitation from mercurous salts, but decomposes into mercury and mercuric sulphide.

Crystallized **mercuric sulphide** HgS occurs as cinnabar, and is red. When formed by precipitation with hydrogen sulphide, or by rubbing together mercury and sulphur, it is black and amorphous. By sublimation, in the course of which it dissociates and recombines, the black form gives the red, crystalline one.

The black and the red varieties do not interact with concentrated acids, or even with boiling nitric acid, which oxidizes most sulphides readily. They are, therefore, still less soluble than is cupric sulphide (pp. 763, 789). They are attacked, however, by *aqua regia,* because of the formation of the negative ion (compare pp. 534, 817) of a complex acid $H_2.HgCl_4$. The red form of the sulphide is used in making paint (**vermilion**). The color is more permanent than that of red lead Pb_3O_4, because reducing gases (*e.g.*, SO_2), acids (*e.g.*, H_2SO_4), and hydrogen sulphide, which are occasionally present in the air, do not affect it. It is not stable, however, when applied to metals, since iron, zinc, etc., all displace mercury from combination, and in these cases red lead is preferred.

Mercuric cyanide $Hg(CN)_2$ is made by treating precipitated mercuric oxide with hydrocyanic acid, and is obtained in square-prismatic crystals. When heated it gives off cyanogen: $Hg(CN)_2 \rightarrow Hg + C_2N_2$, and is a convenient source of this gas (p. 574). The compound is soluble in alcohol, ether, and water. In solution in water it is so little ionized that the freezing-point of the solution is normal (p. 295), and many reagents fail to show the presence of either ion. Thus, with silver nitrate no silver cyanide is precipitated, and with a base no mercuric oxide. With potassium cyanide it forms a complex cyanide $K_2.Hg(CN)_4$. Hydrogen sulphide throws down the sulphide from both the simple and the complex cyanides.

Mercuric fulminate $Hg(ONC)_2$ is obtained as a white precipitate when mercury is treated with nitric acid, and alcohol is added to the solution. It decomposes suddenly when struck, and is used in making percussion caps.

The **thiocyanate** $Hg(NCS)_2$ is precipitated when potassium thiocyanate K(NCS) is added to a solution of mercuric nitrate. When formed into little balls and burned in the air, the substance leaves a curiously voluminous ash (**"Pharaoh's serpents"**).

Ammono-Compounds of Mercury. — When ammonium hydroxide is added to a solution of a mercuric salt, a white substance, of a type which we have not previously encountered, is thrown down. Mercuric chloride gives $Hg(NH_2)Cl$, commonly called "infusible white precipitate," or **ammono-basic mercuric chloride.**

$$HgCl_2 + H.NH_2 + NH_3 \rightarrow Hg(NH_2)Cl + NH_4Cl.$$

The action is similar to an hydrolysis which gives a basic salt: $HgCl_2 + H.OH \rightarrow Hg(OH)Cl + HCl$, excepting that ammonia $H.NH_2$ plays the part of the water. Water gives aquo-basic salts. When liquid ammonia is the solvent, ammono-basic salts are produced. The study of reactions in liquid ammonia solutions by E. C. Franklin has led to the discovery of a large number of new and most interesting substances of this type. In a few cases, as here, an ammono-basic salt is obtained even when water is present.

Mercuric nitrate $Hg(NO_3)_2$ and ammonium hydroxide give an insoluble **ammono-basic mercuric nitrate,** $Hg = N — Hg — NO_3$, which is more basic than the ammono-basic chloride:

$$2Hg(NO_3)_2 + H_3.N + 3NH_3 \rightarrow Hg_2(N)NO_3 + 3NH_4NO_3.$$

The addition of ammonium hydroxide to a solution of potassium mercuri-iodide K_2HgI_4 (which furnishes HgI_2 to the reaction) gives rise to a compound of the same type, ammono-basic mercuric iodide Hg_2NI,H_2O. This appears as a brown precipitate:

$$2HgI_2 + H_3.N + 3NH_3 \rightarrow Hg_2NI + 3NH_4I.$$

A solution of potassium mercuri-iodide containing potassium hydroxide, **Nessler's reagent,** becomes distinctly yellow with traces of ammonia, and brown with larger amounts, and is, therefore, a valuable reagent for detecting traces of this base.

When calomel is treated with ammonium hydroxide, it turns into a black, insoluble body. This is a mixture of free mercury, to which it owes its dark color, and "infusible white precipitate," $Hg + Hg(NH_2)Cl$. To this reaction calomel (Greek καλομέλας, beautiful black) owes its name. Mercurous nitrate also gives a black, insoluble mixture, $2Hg + Hg_2(N)NO_3$.

Calomel, when *dry,* absorbs ammonia gas, forming a molecular compound of the common type $HgCl,NH_3$. This substance loses the ammonia again when the pressure is reduced. The other compounds described above, on the other

hand, do not contain nitrogen and hydrogen in the proportions necessary to form ammonia and are stable. Hence they are necessarily to be regarded as belonging to a different type.

Analytical Reactions of Mercury Compounds. — The two ionic forms of the element, mercurous-ion Hg^{+} and mercuric-ion Hg^{++}, are both colorless. Their chemical behavior is entirely different. Both finally give the black sulphide HgS, which does not interact with acids and other solvents of mercury salts. Mercurous-ion, however, gives an insoluble, white chloride, a black oxide, and a black mixture with ammonium hydroxide, while mercuric-ion gives a soluble chloride, a yellow, insoluble oxide, and a white precipitate with ammonium hydroxide. The behavior with stannous chloride (p. 798) is characteristic. With potassium iodide also the two ions behave differently (pp. 798–9).

More active metals displace mercury from all compounds. Copper is used as the displacing metal, in testing for Hg^{+} or Hg^{++}, because the silvery mercury is easily seen on its surface.

Salts of mercury are volatile. When heated in a tube with sodium carbonate, they give a sublimate of metallic mercury.

Exercises. — 1. Make an equation: (*a*) for the oxidation of ethyl alcohol by heated cupric oxide; (*b*) for the precipitation of cupric sulphide from cupric sulphate solution.

2. When we electrolyzed sodium chloride solution (p. 233), hydrogen was liberated at the cathode. What principle, used in the electrolytic refining of copper, does this phenomenon illustrate?

3. How could you recognize cupric sulphate solution by showing that it contained, (*a*) cupric-ion, (*b*) sulphate-ion?

4. Formulate the action of potassium cyanide in dissolving cupric hydroxide and cuprous sulphide, assuming that potassium cuprocyanide is formed.

5. How should you set about making cupric orthophosphate, ammonium cuprocyanide, and lead cuprocyanide?

6. Write the formulæ of some double salts analogous to potassium-cupric sulphate (p. 790).

7. What chemical reagents are present in a Bunsen flame? If borax beads were made in the oxidizing flame with cupric chloride, cuprous bromide, and cupric sulphate, severally, what actions would take place?

8. Which is the more stable complex ion, $[Cu(CN)_2]^-$ or $[Cu(NH_3)_4]^{++}$? Justify your answer in detail.

9. Formulate, by each of the two methods discussed on pp. 378–9, complete equations for the various oxidation and reduction reactions mentioned in this chapter.

10. Formulate ionic equations to explain, (*a*) why a red precipitate is obtained when an equivalent quantity of potassium iodide solution is added to a soluble mercuric salt, and (*b*) why this precipitate redissolves when an excess of potassium iodide is added (p. 799).

11. To a clear solution of ammonio-cuprous chloride concentrated hydrochloric acid is added, drop by drop, until it is present in large excess. What happens? Explain each stage by means of ionic equations.

12. A precipitate of cuprous chloride is divided into two equal parts. To one ammonia is added until the precipitate just dissolves. To the other potassium cyanide is added until the precipitate just dissolves. In what form is the copper present in each of the two resulting solutions? The two solutions are now mixed. What do you observe? Explain.

13. It is required to connect two points in a city, 5 kilometers apart, with a cable offering a definite electrical resistance. The choice of material lies between drawn copper and 99% aluminium (p. 680). The copper cable would need to have a cross-sectional area of 1 sq. cm.; what would be its weight (p. 785)? What would be the necessary cross-sectional area for the aluminium cable? What would be its weight (p. 769)?

14. An organic substance, known to contain only carbon, hydrogen and oxygen, is analyzed as described on p. 791. 1.046 g. of the substance is found to give an increase in weight of 0.474 g. in the calcium chloride tube, and of 2.316 g. in the vessel containing potassium hydroxide. What percentages of hydrogen and of carbon does the substance contain? What is its empirical formula?

15. What is the percentage loss of weight of malachite (p. 784) when heated in air? Cupric oxide is formed.

16. What is the percentage composition of verdigris (p. 792)?

17. Justify the nomenclature in the case of potassium *cupro*cyanide $KCu(CN)_2$. If potassium *cupri*cyanide did exist, what would be its formula?

18. What is the volume of a flask (p. 795) of mercury, in metric units?

19. What is the weight of 1 liter of mercury vapor at its boiling-point, under atmospheric pressure (p. 796)?

20. What is the density of calomel vapor at 400° and 1 atmosphere, on the basis oxygen = 32?

21. Why does a clear solution of mercurous nitrate become cloudy on warming? Why does addition of dilute HNO_3 make it clear once more? Formulate both cases in detail ionically.

22. You are told that a given solution contains mercury. How would you test whether the element was present in the mercurous or the mercuric state? Give as many tests as possible. If certain of your tests failed to indicate either state, what would you conclude?

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CHAPTER XLVII

SILVER, GOLD AND THE PLATINUM METALS

Although the metals considered in this chapter are located in widely separated groups of the periodic system, they form a natural family of "noble metals."

Silver Ag

Chemical Relations of the Element. — Silver (Ag, atomic number 47) presents a curious assortment of chemical properties. It differs from copper in having a strongly basic oxide, and in giving salts with active acids which are not hydrolyzed by water. In these respects it approaches the metals of the alkalies and alkaline earths. It resembles copper in entering into complex compounds, and in giving insoluble halides. It resembles gold and platinum, in that its oxide is easily decomposed by heat, and in the low position it occupies in the electromotive series and the consequent slight chemical activity of the free metal.

Occurrence. — Native silver, sometimes found in large masses, although more usually scattered through a rocky matrix, contains varying amounts of gold and copper. Native copper always contains dissolved silver. Sulphide of silver Ag_2S occurs alone and dissolved in **galenite** PbS, with which it is isomorphous. Smaller amounts of the metal are obtained from **pyrargyrite** Ag_3SbS_3 and **proustite** Ag_3AsS_3, which are silver sulphantimonite and sulpharsenite, respectively, and from **horn-silver** AgCl. The chief supplies come from the Rocky Mountains, Ontario, and Mexico.

Metallurgy. — The silver contained free, or as sulphide, in ores of copper and lead, is found in the free state dissolved in the metals extracted from these ores, and is secured by refining them. In the electrolytic refining of copper, silver is obtained from the sludge deposited in the baths (p. 794). The proportion present in lead is usually small. **Parke's process,** by which the silver is separated

from the lead, takes advantage of the fact that molten zinc and lead are practically insoluble in one another, while silver is much more soluble in zinc than in lead. The principle is the same as in the removal of iodine from water by ether (p. 220). The lead is melted and thoroughly mixed by machinery with a small proportion of zinc. After a short time the zinc floats to the top, carrying with it in solution almost all of the silver, and solidifies at a temperature at which the lead is still molten. The zinc-silver alloy, largely a compound Ag_2Zn_5, is skimmed off, and heated moderately in a furnace to permit the adhering lead to drain away. The zinc is finally distilled off in clay retorts, and any lead remaining with the silver is removed by **cupellation.** This operation consists in heating the molten metal strongly in a blast of air. The lead is converted into litharge (PbO), which flows in molten condition over the edge of the cupel, and the silver is then cast.

The gold which goes with the silver in Parke's process is separated electrolytically (p. 794). Plates of the silver-gold alloy form the anode, and silver nitrate solution the vat-liquid. The silver, being the more active metal, is ionized and deposited on the cathode, while the gold collects as a powder in a bag surrounding the anode.

Ores of silver which do not contain much or any lead are often smelted with lead ores, and the product is treated as described above, but many other processes are in use. In Mexico the "patio" process has been in use since 1557. The sulphide is converted into chloride by the action of cupric chloride. Metallic mercury displaces the silver: $AgCl + Hg \rightarrow HgCl + Ag$, and, being present in excess, dissolves it. The treatment occupies several weeks, and much mercury is consumed. The amalgam is finally secured by "washing," and the mercury is separated from the silver by distillation.

The world's total output of silver in 1935 was 207,000,000 ounces (troy). The mines of the United States produced 49,000,000 ounces, those of Mexico 70,000,000, and those of Canada 16,000,000.

Physical Properties. — Pure silver is almost perfectly white. It melts at 960°. Its sp. gr. is 10.5. Its ductility is such that wires can be drawn so fine that 2 kilometers weigh only about 1 g. For use in silverware and coins the metal is alloyed with copper to make it harder. In the molten condition it dissolves about twenty-two times its own volume of oxygen, but gives up almost all of this as it solidifies. Fantastically irregular masses result from the "sprouting" or "spitting" which accompanies the escape of the gas.

Silver ornaments have a "fineness" of 800 (80 per cent Ag) or

more. A superficial layer of almost pure-white silver is produced by heating the object in the air and dissolving out the cupric oxide thus formed with dilute sulphuric acid. The surface of the products, if not subsequently burnished, is "frosted." "Oxidized silver" is made by dipping objects made of the metal in a solution of potassium-hydrogen sulphide, whereby a thin film of silver sulphide is produced.

When an electric discharge passes between the ends of two silver wires, held under water, silver is dispersed at the points and forms a *colloidal suspension*. The color of the solution varies from brownish to pink, according to the conditions. Colloidal suspensions of gold and of platinum can be made in the same way (see p. 641).

Chemical Properties. — Silver, when *cold*, is oxidized by ozone, but not by oxygen (see p. 808). It does not ordinarily displace hydrogen from aqueous solutions of acids, but its tendency to form the sulphide is so great that it decomposes hydrogen sulphide and alkali sulphides (see p. 430). Hence, sulphur compounds in the air tarnish the surface, producing Ag_2S, as do also eggs, secretions from the skin (proteins, p. 629), and vulcanized rubber. Silver interacts with cold nitric acid and with hot, concentrated sulphuric acid, giving the nitrate or sulphate of silver and oxides of nitrogen or of sulphur (p. 427). Since its hydroxide has no tendency to behave as an acid, alkalies, whether in solution or fused, have no action upon silver. Hence alkaline substances are heated in vessels of this metal or of iron, rather than in vessels of platinum (p. 817), because platinum is attacked by alkaline materials.

The Halides of Silver. — The **chloride** $AgCl$, **bromide** $AgBr$, and **iodide** AgI are formed as curdy precipitates when a salt of silver is added to a solution containing the appropriate halide ion. The first is white, and melts at about 457°. The second and third are very pale-yellow and yellow respectively. The insolubility in water, which is very great, increases in the above order. The iodide, after melting, solidifies and forms quadratic crystals, which, as they cool, pass at 146° (transition point) into a different physical variety (hexagonal) with evolution of heat (compare p. 799).

When exposed to light, the chloride becomes first violet (colloidal silver, dispersed in the AgCl) and finally brown, chlorine being liberated. The bromide and iodide behave similarly. Solid silver chloride absorbs ammonia, forming with a low pressure $2AgCl,3NH_3$, and with a higher pressure of the gas $AgCl,3NH_3$ (compare

p. 690). The bromide forms no compound in this way, but the iodide yields $2AgI,NH_3$.

In consequence of the progressive insolubility, a cold solution of a bromide will convert the precipitate of silver chloride into bromide, and a soluble iodide will similarly transform the bromide or the chloride into iodide (compare p. 315).

Silver fluoride AgF may be made by treating the oxide or carbonate with hydrofluoric acid: $H_2F_2 + Ag_2O \rightarrow 2AgF + H_2O$. The salt is very soluble and deliquescent.

Complex Compounds of Silver. — Silver chloride dissolves easily in excess of ammonium hydroxide, giving the complex cation $Ag(NH_3)_2^+$. The bromide, which dissolves less readily, gives the same complex ion. **Ammonio-argentic-ion** $Ag(NH_3)_2^+$, in solutions of concentrations such as are commonly used (0.1 *N* to *N*), dissociates sufficiently to give a smaller concentration of silver-ion Ag^+ than does a saturated solution of the bromide, but much more than the highly insoluble iodide (compare p. 789). Hence the latter dissolves only very slightly in ammonium hydroxide, and can be precipitated in ammoniacal solution. All three of the insoluble halides dissolve in solutions of potassium cyanide and of sodium thiosulphate, as do also all the other insoluble silver salts. Usually an equivalent amount of the cyanide or thiosulphate suffices, but for solution of the sulphide an excess is required. With the cyanide, double decomposition gives first the insoluble silver cyanide AgCN which then interacts forming the soluble **potassium argenticyanide** $K.Ag(CN)_2$. The thiosulphate gives a solution from which crystals of a complex salt $Na_3.Ag(S_2O_3)_2,2H_2O$ are obtained. The complex anion in the solution appears to be $Ag(S_2O_3)_2^{\equiv}$.

The more active metals, like zinc and copper, displace silver from all solutions, whether the solutions contain simple or complex salts.

The increase in the solubility of silver chloride, when sodium chloride is added to its saturated solution (p. 758), must be regarded as due to the formation of complex ions of the types $AgCl_2^-$, $AgCl_3^=$ etc., corresponding to complex salts $Na.AgCl_2$, $Na_2.AgCl_3$, etc., which are too soluble to be isolated directly from the solution. It is highly interesting to note that, if we compare the effect of equivalent solutions of different metallic chlorides upon the solubility of silver chloride, we find that *the increase in solubility is greater the higher the position, in the electromotive series, of the positive radical.* The results obtained from other systems lead to the general rule that the stability of a molecular compound of the type RX,R^1X increases uniformly with the diversity in character of R and R^1, the basis of diversity being the positions of R and R^1 in the electrode potential series (p. 313). The more

stable the compound, the less it tends to break up into its simpler constituents, and consequently the greater the increase in solubility when one of these constituents is, as in the case of silver chloride, an insoluble salt.

Oxides of Silver. — When sodium hydroxide is added to a solution of a salt of silver, a pale-brown precipitate is obtained, which, after being freed from water, is found to be Ag_2O. We should expect to obtain the hydroxide $AgOH$ in this fashion, but it appears to be unstable. The aqueous solution of argentic oxide, however, is distinctly alkaline, and presumably therefore does contain the hydroxide: $2AgOH \rightleftarrows Ag_2O + H_2O$. Silver oxide is also formed by boiling silver chloride with caustic potash. Since the oxide is much more soluble than the chloride (see table), we should expect the reverse of the above action to be the normal one. Here, however, the presence of potassium-ion favors the formation of complex chlorides and reverses the relations in regard to solubility.

Argentic oxide is an active basic oxide, and all the salts of silver are derived from it. When moist, it absorbs carbon dioxide from the air. Its solutions show concentrations of hydroxyl-ion smaller, it is true, than equimolar solutions of the active bases, but considerably greater than similar solutions of ammonium hydroxide (p. 318). With ammonium hydroxide it forms the soluble ammonio-argentic hydroxide $Ag(NH_3)_2.OH$, which is as active a base as is potassium hydroxide. The solution, when allowed to evaporate, deposits black crystals of an explosive substance whose composition has not been determined.

When the oxide is heated, it gives off oxygen, leaving metallic silver. The action is reversible (G. N. Lewis) and the dissociation pressure of the oxygen is 20.5 atmospheres at 302°.

Silver **peroxide** Ag_2O_2 is formed by the action of ozone on silver. In the electrolysis of silver nitrate a deposit of shining black crystals which contain some silver peroxide is formed on the anode.

Salts of Silver. — Silver nitrate $AgNO_3$ is obtained by treating silver with dilute nitric acid:

$$3Ag + 4HNO_3 \rightarrow 3AgNO_3 + NO + 2H_2O.$$

From the solution, colorless rhombic crystals (Fig. 13, p. 31) are deposited. These melt at 212°. Thin sticks made by casting (lunar caustic) are used to cauterize sores, because the substance combines with proteins to form insoluble compounds. The aqueous solution

is *neutral.* The pure salt is not affected by light, but when deposited on cloth, on the skin of the fingers, or on the mouth of the reagent bottle, it is reduced by organic matter, and silver is liberated. For this reason it is an ingredient in some **marking-inks.**

Silver carbonate (the neutral salt Ag_2CO_3, and not a basic carbonate) is precipitated from solutions of salts of silver by soluble carbonates. It is slightly yellow in color. With water it gives a faint alkaline reaction and, like calcium carbonate, is soluble in excess of carbonic acid (p. 729). When heated, the carbonate decomposes, leaving metallic silver. The **sulphate** Ag_2SO_4 is made by the action of concentrated sulphuric acid on the metal. When it is mixed with a solution of aluminium sulphate (see p. 774) octahedral crystals of **silver-alum** $Ag_2SO_4,Al_2(SO_4)_3,24H_2O$ are obtained. **Silver sulphide** Ag_2 is precipitated by hydrogen sulphide from solutions of all silver compounds, whether free acids are present or not, and irrespective of the form in which the silver is combined. *Excess* of potassium cyanide, however, prevents its precipitation from the argenticyanide. The sulphide is formed by the action of metallic silver on alkaline hydrosulphides, and this interaction forms the basis of the "hepar" test for sulphur (p. 430).

Silver **orthophosphate** Ag_3PO_4 (yellow), **arsenate** Ag_3AsO_4 (brown), and **chromate** Ag_2CrO_4 (crimson) are produced by precipitation, and their distinctive colors enable us to use silver nitrate in analysis as a reagent for identifying the acid radicals.

Electroplating. — The process is similar to the electro-deposition of copper (p. 793). The article to be plated is cleaned with extreme care and made the negative electrode. A plate of silver forms the positive electrode and, since simple salts of silver do not give coherent deposits, the bath is a solution of potassium argenticyanide. The potassium-ion K^+ migrates to the negative electrode and, since potassium requires a much greater electromotive force for its liberation than does silver (compare p. 233), silver is there deposited from the trace of argentic-ion given by the complex silver ions in the neighborhood:

$$Ag(CN)_2^- \leftrightarrows Ag^+ + 2CN^-, Ag^+ + \ominus \rightarrow Ag^0.$$

At the positive electrode silver goes into solution in equivalent amount, giving argentic-ion, and the above equations are reversed.

Mirrors are silvered through the reduction of ammonio-silver

nitrate by organic compounds such as formaldehyde CH_2O (formalin) or grape sugar:

$$4AgOH + CH_2O \rightarrow 3H_2O + 4Ag\downarrow + CO_2.$$

The film of silver is washed, dried, and varnished.

Photography. — The taking of a photograph involves four processes — preparation of the plate, exposure, development, and fixing. In preparing the plate, silver bromide is first precipitated in water containing gelatine. The mixture is kept warm, to permit the precipitate to become more sensitive to light by acquiring a coarser grain ("ripening"). The "emulsion" is applied to plates of glass or strips of transparent celluloid (films).

The brief **exposure** of the plate to the image of the object, well-focussed in the camera, produces no visible effect. But the bromide is thereafter more easily reduced to metallic silver, in proportion to the intensity of the light that fell upon each part.

Development consists in applying a reducing agent, of such slight activity that its effect during the process on non-illuminated parts of the bromide is practically zero. Ferrous oxalate, or an alkaline solution of pyrogallol $C_6H_3(OH)_3$ or of quinol $C_6H_4(OH)_2$ (two substances belonging to the class of phenols, see p. 587), may be used. The reduction goes fastest and deposits most silver where the illumination was most intense. Thus, the plate becomes most opaque where the object was brightest, and *vice versa*. On account of this reversal, the plate is called a *negative*. With the potassium salt of quinol, quinone $C_6H_4O_2$ is formed:

$$2AgBr + C_6H_4(OK)_2 \rightarrow 2Ag + 2KBr + C_6H_4O_2.$$

The foregoing processes are all carried out in a faint red light, which is almost without action on silver bromide. To prevent the gradual reduction of the remaining, unchanged bromide to silver by daylight, it is dissolved out by soaking the plate in sodium thiosulphate (**fixing**). The plate is now *clear* where no silver was deposited. The negative is finally washed thoroughly to remove all except the gelatine and the silver image, and is then dried.

In **printing,** the prepared paper is illuminated *through* the negative, and light and dark are again reversed. The denser parts of the negative protect the paper below them, and leave these parts white. On *printing paper,* silver chloride suspended in egg albumen is the sensitive substance, and the silver is liberated in a reddish,

colloidal condition. The color is improved by **toning** with a solution containing gold chloride, as part of the silver goes into solution and gold (purplish) is deposited in its place. The print is fixed with sodium thiosulphate, washed, and dried. Papers like **velox** (invented by Baekeland) are essentially like plates (silver bromide in gelatine), and are exposed, developed, and fixed in the same way.

We have already seen (p. 599) that light of short wave-length — blue and violet — has the greatest effect upon silver halides. The time, in seconds, required for equal effects is approximately: violet 15, blue 29, green, 37, yellow 330, red 600. Hence objects showing to the eye a variety of colors are entirely misrepresented, as regards the relative brightness of their parts, by photography. Now the important fact, in this connection, is that only that part of the light which is absorbed in traversing the film, and not that which is scattered or transmitted, can be used for chemical change. Hence, dipping plates in solutions of substances capable of absorbing yellow and red radiations causes them to absorb more of the energy of these photographically weakest radiations, and to give greater chemical action in response to them. This partially restores the balance. Such plates are called **orthochromatic,** and are backed with substances like eösin (used also in making red ink) or cyanine.

Analytical Reactions of Silver Compounds. — Argentic-ion Ag^+ is colorless. Many of its compounds are insoluble, the precipitation of the chloride, which is insoluble in dilute acids, being used as a test. Mercurous chloride and lead chloride are also white and insoluble, but silver chloride dissolves in ammonium hydroxide, mercurous chloride turns black, and lead chloride is not altered in color (and is also soluble in hot water). With excess of ammonium hydroxide, silver salts give the complex cation $Ag(NH_3)_2^+$ and, from solutions containing silver in this form, only the iodide and sulphide can be precipitated. Sodium thiosulphate and potassium cyanide dissolve all silver salts, giving salts of complex acids with silver in the anion (p. 807).

Gold Au

Chemical Relations of the Element. — Gold (Au, at. wt. 197.2) forms two very incomplete series of compounds corresponding respectively to aurous and auric oxides, Au_2O and Au_2O_3. The former is a feebly basic oxide, the latter mainly acid-forming. No simple salts with oxygen acids are stable. All the compounds of gold are easily decomposed by heat with liberation of the metal. All other common metals displace gold from solutions of its compounds (p. 313). Mild reducing agents likewise liberate gold. The element enters into many complex anions.

Occurrence and Metallurgy. — Gold is found chiefly in the free condition disseminated in veins of quartz, or mixed with alluvial sand. Small quantities are found also in sulphide ores of iron, lead, and copper. Telluride of gold (**sylvanite**), in which silver takes the place of part of the gold $[Au,Ag]Te_2$,* is found in Colorado. This mineral when heated loses its tellurium, and gold, alloyed with silver, remains.

In **vein mining** (*e.g.*, in the Transvaal) the rock is pulverized with iron stamps working in an iron trough. The powder is washed in the form of mud over plates of copper amalgamated with mercury, in which about 55 per cent of the gold dissolves. The amalgam is afterwards scraped off, the mercury removed by distillation, and the gold residue refined. The tailings still contain 45 per cent of the gold, adhering to the particles of rock. They are covered with sodium cyanide solution, and exposed to the air, until the gold has been dissolved as sodium aurocyanide $NaAu(CN)_2$. From this solution the gold is deposited by electrolysis, or displaced by zinc.

The alluvial deposits are washed, on a small scale, in "cradles" (shallow pans) and, on a large scale, by being carried by water down a long trough (**placer mining**). The gold, having a much higher specific gravity than the rock, sinks to the bottom, while the rock particles are carried away. In the trough the gold settles between cleets nailed across the bottom. In **hydraulic mining,** a modification of placer mining, very heavy streams of water are thrown against the deposit.

In 1935, the gold production of the world exceeded $1,000,000,000 in value. $360,000,000 of this came from the Transvaal, $115,000,000 from Canada, and $110,000,000 from the United States. The recent increase in the value of gold to $35 per fine ounce has caused many mines producing low-grade ore, previously shut down, to be re-opened.

Properties. — Gold is yellow in *color*. It is the most malleable and *ductile* of metals. It *melts* at 1063°. To enable it to resist wear, it is alloyed (in coinage and jewelry) with copper or silver. Its chief use is for storage in treasury vaults, but it is interesting

* Amongst minerals, mixed crystals of isomorphous salts are so commonly found that formulæ like the above are constantly used by mineralogists. $[Au,Ag]Te_2$ indicates a mixture in varying proportions of the isomorphous tellurides $AuTe_2$ and $AgTe_2$.

to note that all of the metal mined since the beginning of history could be accommodated in a single cube with a side of forty feet. The proportion of gold in the alloys is defined in **karats.** Pure gold is "24 karat" fine. British gold coins are 22 karat, and American coins 21.6 karat (90 per cent gold).

Gold is not affected by free oxygen nor by hydrogen sulphide. It does not displace hydrogen from dilute acids, nor does it interact with nitric or sulphuric acids or any oxygen acids except selenic acid. It combines, however, with free chlorine and bromine. It interacts with a mixture of nitric and hydrochloric acids (*aqua regia*), giving chlorauric acid $H.AuCl_4$. This happens, not because *aqua regia* is more active (contains a higher concentration of H^+) than either of the acids taken alone, but because it furnishes both the chloride-ion Cl^- and the oxidizing agent required to produce the exceedingly stable (little dissociated) anion $AuCl_4^-$. Chlorine-water dissolves gold also, for the same reason (see p. 372). Gold is the least active of the familiar metals.

Compounds with the Halogens. — **Chlorauric acid,** formed as above, is deposited in yellow, deliquescent crystals of $H.AuCl_4, 4H_2O$. The yellow sodium chloraurate $NaAuCl_4, 2H_2O$, obtained by neutralization of the acid, is used in photography (p. 811). The acid gives up hydrogen chloride when heated very gently, leaving the red, crystalline **auric chloride** $AuCl_3$. When auric chloride is heated to 180° **aurous chloride** AuCl and chlorine are formed. This salt is a white powder. It is insoluble in water, but in boiling water is converted quickly into auric chloride and free gold: $3AuCl \rightarrow AuCl_3 + 2Au$. When potassium iodide is added to a solution of chlorauric acid, or to sodium chloraurate, the yellow **aurous iodide** is precipitated:

$$NaAuCl_4 + 3KI \rightarrow NaCl + AuI\downarrow + I_2 + 3KCl.$$

The action is like that on cupric salts (p. 788), and for a similar reason, namely, that auric iodide is not stable.

Other Compounds. — When caustic alkalies are added to chlorauric acid, or to sodium chloraurate, **auric hydroxide** $Au(OH)_3$ is precipitated. This substance is a weak acid, and interacts with excess of the base, forming **aurates.** These are derived from meta-auric acid ($H_3AuO_3 - H_2O = HAuO_2$), as, for example, **potassium aurate** $K.AuO_2, 3H_2O$. This salt interacts by double decomposition,

giving, for instance, with silver nitrate, the insoluble **silver aurate** $AgAuO_2$. **Auric oxide** Au_2O_3 is a brown, and **aurous oxide** Au_2O is a violet powder. With hydrochloric acid the latter gives chlor-auric acid and free gold.

On account of its reducing action, hydrogen sulphide precipitates from chlorauric acid a dark-brown mixture containing much **aurous sulphide** Au_2S and free sulphur, as well as some **auric sulphide** Au_2S_3. The sulphides interact with alkali sulphides, giving complex **sulphaurites** and **sulphaurates,** such as K_3AuS_2 ($= 3K_2S, Au_2S$) and $KAuS_2$ ($= K_2S,Au_2S_3$), which are soluble (p. 687, and see Tin, Arsenic, and Antimony).

The **aurocyanides** like $K.Au(CN)_2$, and the **auricyanides,** like $K.Au(CN)_4$, are formed by the action of potassium cyanide on aurous and auric compounds, respectively. They are colorless and soluble. Their solutions are used as baths, in conjunction with a gold anode, for electro-gilding.

It will be seen that gold, although physically a metal, is chemically on the whole a *non-metallic* element.

Assaying. — In assaying a sample to determine its gold content, the finely-crushed material is heated with borax and lead in a small crucible (cupel) of bone ash. The lead and copper are oxidized, and their oxides are absorbed by the cupel, leaving a drop of molten alloy of gold and silver. The cold button is flattened by hammering and rolling, and treated with nitric acid to remove the silver. The gold, which remains unattacked, is washed, fused again, and weighed. The acid will not interact with the silver, and remove it completely, if the quantity of gold exceeds 25 per cent. When the proportion of gold is greater than this, a suitable amount of pure silver is fused with the alloy (**"quartation"**).

The principles behind quartation have recently been elucidated by Tammann, as the result of a study of the crystal structure of gold-silver alloys. Both of these metals exhibit a cubic-lattice arrangement of atoms (see p. 67) and form solid solutions with each other by orderly replacement of atoms in the unit cubes. Now if gold constitutes *more than one-quarter* of the atoms in such a cubic lattice, then, after the surface silver atoms have been removed by an acid, there will remain a "united front" of gold atoms, which prohibits further corrosion. But if *less than one-quarter* of the atoms are gold, the formation of a coherent barrier is impossible, and the alloy will be completely disintegrated by the acid.

The Platinum Metals

The rare elements of Mendelejeff's eighth group divide themselves into sets of three each. **Ruthenium** (Ru, atomic number 44), **rhodium** (Rh, at. no. 45), and **palladium** (Pd, at. no. 46) have specific gravities from 12.26 to 11.5. Similarly **osmium** (Os, at. no. 76), **iridium** (Ir, at. no. 77), and **platinum** (Pt, at. no. 78) form a triad with specific gravities from 22.5 to 21.5. Chemically, ruthenium shows the closest resemblance to osmium, and both are allied to iron. Similarly, rhodium and iridium, and palladium and platinum, are natural pairs.

The six elements are found alloyed in nuggets and particles which are separated from alluvial sand by washing. Platinum forms 60–84 per cent of the whole. The chief deposits are in the Ural Mountains, Colombia, and the Transvaal. Large quantities of the platinum metals are also recovered in the refining of nickel-copper matte from the Sudbury district of Ontario (p. 913). The components are separated from each other by a complex series of chemical operations.

Ruthenium and Osmium. — These metals are gray like iron, while the other four are whiter and more like cobalt and nickel. They also resemble iron in being the most infusible members of their respective sets. Both melt considerably above 2000°. They likewise resemble iron in uniting easily with free oxygen, while the other four elements do not. Ruthenium gives RuO_2 and even RuO_4, although the latter oxide is more easily obtained indirectly. Osmium gives OsO_4, **"osmic acid,"** a white crystalline body melting at 40° and boiling at about 100°. The odor and irritating effects of the vapor recall chlorine (Greek, ὀσμή, odor). The substance is not really an acid, nor even an acid anhydride. The aqueous solution is used in histology, and stains tissues in consequence of its reduction by organic bodies to metallic osmium. Osmium forms also a yellow, crystalline **fluoride,** OsF_8 (m.-p. 34.5°). It will be observed that ruthenium and osmium have a maximum valence of eight.

These elements resemble iron (p. 894) in giving ruthenates and osmates, like K_2RuO_4 and K_2OsO_4, but no corresponding oxide or acid. **Potassium ruthenate** resembles potassium manganate (p. 889) and gives, when diluted, an oxide of ruthenium and **potassium perruthenate** $KRuO_4$. There are also salts derived from the oxides Ru_2O_3 and Os_2O_3.

Rhodium and Iridium. — These metals are not attacked by *aqua regia,* while the other four are dissolved, more or less slowly. They are harder than platinum, and iridium is alloyed with this metal for the purpose of increasing its hardness (*e.g.*, in pen-points), and its resistance to the action of fluorine. A platinum-iridium alloy is used for the international standards of length and mass, kept in Paris. A thin film of rhodium, electro-plated on silver-ware, preserves it from tarnish.

Rhodium and iridium resemble cobalt in having no acid-forming properties. Salts corresponding to the oxides Rh_2O_3 and Ir_2O_3 are formed, and iridium gives compounds derived from IrO_2 as well. The most familiar compounds of iridium are **complex chlorides** such as K_3IrCl_6 ($= 3KCl,IrCl_3$) and K_2IrCl_6 ($= 2KCl,IrCl_4$). The solutions of the latter are red, and the acid, **chloro-iridic acid** H_2IrCl_6, is often found in commercial chloroplatinic acid H_2PtCl_6, and confers upon it a deeper color.

Palladium and Platinum. — Palladium is the only metal of this family which is attacked by nitric acid. Palladium and platinum form *-ous* and *-ic* compounds of the forms $PdCl_2$ and $PdCl_4$, respectively. The oxides PdO and PtO and the corresponding hydroxides are basic. When quadrivalent, the metals appear chiefly in complex compounds, like $H_2.PtCl_6$, $H_2.PdCl_6$, in which the metal is in the anion. Platinum gives also platinates derived from the oxide PtO_2, but quadrivalent platinum furnishes no well defined salts in which it constitutes by itself the positive ion.

Palladium. — This metal (m.-p. 1555°), named from the planetoid Pallas, is noted chiefly for its great tendency to adsorb hydrogen. When finely divided, it takes up about 800 times its own volume. The amount adsorbed varies continuously with the concentration (pressure) of the hydrogen, although not according to a uniform rule, and the product is in part at least a solid solution (**occlusion**). When a strip of palladium is made the cathode of an electrolytic cell, over 900 volumes of hydrogen may be occluded. This adsorbed hydrogen, in consequence of the catalytic influence of the metal, reacts more rapidly than does the gas, and consequently a strip of hydrogenized palladium will quickly precipitate, from solutions of their salts, copper and other metals less electropositive than hydrogen and will reduce ferric and other reducible salts:

$$Cu^{++} + H_2 \rightarrow 2H^+ + Cu.$$
$$2Fe^{+++} + H_2 \rightarrow 2Fe^{++} + 2H^+.$$

A palladium-gold alloy (**palau**) has recently been devised as a substitute for platinum in laboratory crucibles.

The **palladious salts** are such as $PdCl_2$, $PdSO_4$, $Pd(NO_3)_2$. Palladic chloride, formed by treating the metal with *aqua regia*, is contained in the solution in the form of chloropalladic acid H_2PdCl_6 ($= 2HCl,PdCl_4$) and gives difficultly soluble salts like K_2PdCl_6. When the solution of the acid is boiled, however, chlorine is given off and $PdCl_2$ or H_2PdCl_4 remains in solution.

Platinum. — This metal (Spanish *plata*, silver) is grayish-white in color, and is very ductile. At a red heat it can be welded. It does not melt in the Bunsen flame, but fuses easily in the oxy-hydrogen jet (m.-p. 1755°). On accounts of its very small chemical activity it is used in electrical apparatus and for making wire, foil, crucibles and other vessels for use in laboratories. It unites, however, with carbon, phosphorus, and silicon, becoming brittle, and forms fusible alloys with metals like antimony and lead. Hence care has to be taken not to heat in vessels made of it compounds from which these elements may be liberated. It also interacts with fused alkalies, giving platinates, but the alkali carbonates may be melted in vessels of platinum with impunity. The oxygen acids are without action upon it, but on account of the tendency to form the extremely stable complex ion $PtCl_6^{=}$ (p. 534), the oxidizing agents and chloride-ion in *aqua regia* convert it into **chloroplatinic acid** H_2PtCl_6.

This reaction may be analyzed by the ion-electron method (p. 379) as follows:

$$Pt + 6Cl^- \rightarrow PtCl_6^{=} + 4\ominus$$
$$4NO_3^- + 8H^+ + 4\ominus \rightarrow 4NO_2 + 4H_2O$$

Adding: $Pt + 6Cl^- + 4NO_3^- + 8H^+ \rightarrow PtCl_6^{=} + 4NO_2 + 4H_2O$

In full: $Pt + 6HCl + 4HNO_3 \rightarrow H_2PtCl_6 + 4NO_2 + 4H_2O.$

The metal adsorbs oxygen upon its surface and also "occludes" hydrogen. The finely divided forms of the metal, such as **platinum sponge** made by igniting ammonium chloroplatinate $(NH_4)_2PtCl_6$, **platinum black** made by adding zinc to chloroplatinic acid, and **platinized asbestos** made by dipping asbestos in a solution of chloroplatinic acid and heating it, show this behavior very conspicuously. They cause instant explosion of a mixture of oxygen and hydrogen, in consequence of the heat developed by the rapid union of that part of the gases which is adsorbed by the metal. A heated spiral

of fine platinum wire will continue to glow if immersed in the mixture of methyl alcohol vapor and air (oxygen), which exists above a little of the alcohol in the bottom of a beaker. Some gas-lighters work on this principle. The heat is developed by the interaction between the substances, which takes place with great speed at the surface of the platinum. Specially prepared platinum is used as a contact agent in making sulphur trioxide (p. 420) and in ammonia oxidation (p. 531).

Platinum has approximately the same coefficient of expansion as glass, and was formerly employed in incandescent bulbs to furnish the electrical connection with the filament in the interior. Cheaper substitutes, however, have now been devised for this purpose. Large amounts are consumed in photography and by dentists. The metal is employed most extensively, however, for jewelry and in chemical catalytic processes.

On account of the increasing supply, platinum is now (1937) worth only $50.00 per ounce troy, or slightly more than gold (nominally $35.00 per ounce). The world's production in 1935 was approximately 300,000 ounces (troy).

Compounds of Palladium. — **Platinous chloride** $PtCl_2$ is made by passing chlorine over finely divided platinum at 240–250° or by heating chloroplatinic acid to the same temperature. It is greenish and insoluble in water, but forms with hydrochloric acid the soluble **chloroplatinous acid** H_2PtCl_4. Potassium chloroplatinite K_2PtCl_4 is used in photography in making platinum prints (compare p. 813). Bases precipitate black **platinous hydroxide** $Pt(OH)_2$ which interacts with acids but not with bases. Gentle heating gives the **oxide** PtO and stronger heating the metal. With potassium cyanide and barium cyanide soluble **platino-cyanides,** $K_2Pt(CN)_4,3H_2O$ and $BaPt(CN)_4,4H_2O$, are formed. These substances, when solid, show strong fluorescence, converting X-rays as well as ultra-violet rays into visible radiations. The barium salt is used on screens to receive the shadows cast by X-rays.

Platinic chloride $PtCl_4$ may be made by treating the metal with *aqua regia* and heating the **chloroplatinic acid** H_2PtCl_6 so obtained in a stream of chlorine at 360°. **Chloroplatinic acid** forms reddish-brown deliquescent crystals $H_2PtCl_6,6H_2O$. With potassium and ammonium salts, it yields the sparingly soluble, yellow chloroplatinates K_2PtCl_6 and $(NH_4)_2PtCl_6$ (see pp. 705, 710), in solutions of which the platinum migrates towards the anode and silver salts precipitate Ag_2PtCl_6 and not silver chloride.

Bases interact with chloroplatinic acid, giving a yellow or brown precipitate of **platinic hydroxide** $Pt(OH)_4$. This substance interacts both with acids and with bases. In the latter case **platinates,** like $Na_2H_{10}Pt_3O_{12},H_2O$, have been obtained. Both sets of platinum compounds interact with hydrogen sulphide, giving the **sulphides,** PtS and PtS_2. These are black powders which interact with yellow ammonium sulphide solution giving ammonium sulphoplatinates.

Exercises. — 1. Make equations for: (*a*) the action of concentrated sulphuric acid on silver; (*b*) the decomposition of silver chloride by light.

2. Make equations for: (*a*) the displacement of gold from potassium chloraurate by silver; (*b*) the decomposition of chloroplatinic acid, and of (*c*) ammonium chloroplatinate by heat; (*d*) the action of zinc on chloroplatinic acid.

3. What would be the advantages and disadvantages of using gold instead of platinum for crucibles?

4. Explain in detail why silver iodide will not dissolve in ammonium hydroxide, why silver bromide goes into solution with some difficulty, and why silver chloride dissolves readily.

5. Justify the nomenclature in the cases of potassium aurocyanide $KAu(CN)_2$ and potassium auricyanide $KAu(CN)_4$ by deducing the valence of gold in each (p. 383).

6. What reagents should you use to precipitate the phosphate, arsenate, and chromate of silver? Write the ionic equations.

7. Write the equations for the interactions of, (*a*) potassium hydroxide and auric hydroxide, (*b*) potassium cyanide and sodium chloraurate.

8. In what respects are the elements of this chapter distinctly metallic, and in what respects are they allied to the non-metals (pp. 440–1)?

9. Of which metals should it be possible to obtain colloidal suspensions in water, and of which not (p. 142)? Suggest some liquids in which you should expect to obtain colloidal suspensions of the alkali metals.

10. What are the relative solubilities of silver iodide and silver fluoride in water at 18° (see Table on inside front cover), expressed in normalities?

11. Which is the most stable of all the complex ions of silver mentioned on p. 807?

12. Balance the following equations by the ion and electron method:

(*a*) $Ag + HNO_3 \rightarrow AgNO_3 + NO + H_2O$.
(*b*) $AgBr + FeSO_4 \rightarrow Ag + Fe_2(SO_4)_3 + FeBr_3$.
(*c*) $NaCN + Au + O_2 + H_2O \rightarrow NaAu(CN)_2 + NaOH$.

13. To 100 c.c. of the best distilled water 2 c.c. of a 1 per cent solution of gold chloride are added. In another 100 c.c. of distilled water, 0.5 g. of tannin (a reducing agent, p. 909) is dissolved. The two solutions are heated, and the second added to the first in successive proportions. What do you observe? Explain.

14. Tabulate the reactions you have met with, in this and preceding chapters, in which a metal of the platinum group functions as a catalyst.

15. Correlate the uses of platinum with its physical and chemical properties.

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CHAPTER XLVIII

TIN AND LEAD

The elements on the right side of the fifth column of the periodic table, aside from carbon and silicon, are **germanium** (Ge, atomic number 32), **tin** (Sn, at. no. 50), and **lead** (Pb, at. no. 82). **Titanium** (Ti, at. no. 22), **zirconium** (Zr, at. no. 40), **cerium** (Ce, at. no. 58), **hafnium** (Hf, at. no. 72), and **thorium** (Tt, at. no. 90) occupy the left side.

Cerium, it may be noted, belongs legitimately to this family only in its quadrivalent state, the *ceric* salts. The exterior electron arrangement of its atom is here 2, 8, 18, 18, 8, 4. In the trivalent *cerous* salts the element functions as a rare earth, with an electron arrangement 2, 8, 18, 19, 8, 3 (see p. 499).

The Chemical Relations of the Family. — The elements on the right side will first be considered. All of these elements show a maximum valence of four, but germanium, tin, and lead are also bivalent. In this respect they resemble carbon and differ from silicon, which is more closely allied to the elements on the left side of the column. The oxides and hydroxides in which these three elements are bivalent become more basic, and the elements themselves more metallic in chemical relations, with increase in atomic weight. Curiously enough, the same three hydroxides are also acidic. They are more strongly acidic than is zinc hydroxide, for the salts they form by interaction with bases are less hydrolyzed than are the zincates. This acidic character likewise increases in the order in which the elements are named above.

GERMANIUM Ge

Germanium (see p. 448) may be described as a transition element between carbon and tin. It forms two oxides GeO and GeO_2 corresponding to those of carbon and of tin. **Germanious oxide** is not very definitely basic or acidic, and the sulphide is the only other

well-defined compound of this set. **Germanic oxide** and hydroxide are acidic entirely. The resemblance to carbon is shown in the formation of a series of hydrides beginning with the colorless gas **monogermane** GeH_4, and of halogen derivatives thereof such as **germano-chloroform** $GeHCl_3$. Like carbon, tin, and silicon, germanium gives a volatile **chloride** $GeCl_4$ (b.-p. 86°). Like tin and gold (p. 814), it forms **complex sulphides** derived from germanic sulphide, such as K_2GeS_3. The element was discovered (in 1886, see p. 448) in **argyrodite,** a complex sulphide $4Ag_2S, GeS_2$. It has been discovered recently that the ash of many varieties of coal contains up to one per cent of germanium oxide.

Tin Sn

The Chemical Relations of the Element. —Tin is both bivalent and quadrivalent. The only known hydride, SnH_4, is a gas which rapidly decomposes when heated. Each of the hydroxides, $Sn(OH)_2$ and $SnO(OH)_2$ (or $Sn(OH)_4$), is both basic and acidic, so that there are really four series of compounds. Still, stannous hydroxide is mainly a base, of a feeble sort, while stannic hydroxide is mainly an acid. Thus we have stannous chloride, sulphate, and nitrate, which are stable, although they are all more or less hydrolyzed by water, and sodium stannite Na_2SnO_2 which is unstable. On the other hand, stannic nitrate, sulphate, and chloride are completely hydrolyzed by water, while sodium stannate Na_2SnO_3 is comparatively stable. The dioxide SnO_2 is an infusible solid, and resembles, therefore, silicon dioxide. Tin has a tendency to give complex acids and salts, like H_2SnCl_6, $(NH_4)_2SnCl_6$, H_2SnI_6, K_2SnF_6, but these are quite appreciably dissociated in solution, giving ions of Sn^{++++}. Tin forms no salts with weak acids, like carbonic acid.

Occurrence and Extraction. — Tin has long been in use, specimens of it being found in Egyptian tombs. The chief ore of tin is **tin-stone,** or **cassiterite** SnO_2, which consists of square prismatic crystals whose dark color is due to the presence of iron compounds. The ore is roughly pulverized and washed, to remove granite or slate with which it is mixed, and is then roasted, to oxidize the sulphides of iron and copper, and drive off the arsenic which it contains. After renewed washing to eliminate sulphate of copper and oxide of iron, it is reduced with coal in a reverberatory furnace

(p. 898). The tin is afterwards remelted at a gentle heat, and the pure metal which flows away from compounds of iron and arsenic is cast in blocks (**block tin**). Formerly the mines in Cornwall (England) constituted the chief source of the metal, but now the largest supply comes from the Malay States, the next largest from Bolivia. The average total production (restricted) is 140,000 metric tons annually.

Physical and Chemical Properties. — Tin is a silver-white, crystalline metal of low tenacity but great malleability (tin-foil). Its specific gravity is 7.31, and its melting-point about 232°.

Tin, although it displaces hydrogen from dilute acids, is not tarnished by moist air. With warm hydrochloric acid it gives stannous chloride $SnCl_2$ and hydrogen. Hot, concentrated sulphuric acid forms stannous sulphate $SnSO_4$ and sulphur dioxide. Nitric acid, when cold and very dilute, interacts with it, giving stannous nitrate, and a portion of the nitric acid is reduced to ammonia (compare p. 532):

$$4Sn + 10HNO_3 \rightarrow 4Sn(NO_3)_2 + 3H_2O + NH_4NO_3.$$

With concentrated nitric acid, stannic nitrate is first formed, but most of this salt is hydrolyzed by the water at the high temperature of the action (compare p. 685), and metastannic acid H_2SnO_3 (see, however, p. 826) remains. The final result is therefore:

$$Sn + 4HNO_3 \rightarrow H_2SnO_3 + 4NO_2 + H_2O.$$

Tin also displaces hydrogen from caustic alkalies, giving metastannates, such as sodium metastannate Na_2SnO_3.

In 1851, the tin pipes of an organ were found to have turned largely into a gray powder. In 1868 a shipment of blocks of tin stored in the custom house in Leningrad was found to have changed in the same way. Objects of tin in museums frequently show spots indicating the presence of the "tin pest," as it is called. It now appears that white, metallic tin is stable only above 18°, and that below this temperature it is unstable and is liable to change into gray tin of lower density (5.75). This transition point is similar to that of sulphur at 96° (p. 400).

Uses. — Tin-plate, used in making "tin cans," is produced by dipping carefully cleaned sheets of mild steel into molten tin. So long as the layer of tin remains intact, the iron is protected from rusting. But, if the tin layer is damaged, the tin (see p. 850)

actually hastens the rusting of the iron. Vessels of copper are also coated, internally, with tin, to prevent the formation of the basic carbonate (p. 785). For this purpose they are cleaned with ammonium chloride, sprinkled with rosin (to reduce the oxide), and heated to 230°. Molten tin is then spread on the surface with a piece of tow. Common pins are made of brass wire, and are coated with tin by being shaken in a solution containing a salt of this metal. The zinc in the alloy displaces some of the tin, and this is deposited on the surface of the brass. Alloys of tin, such as **bronze** (p. 786), **soft solder** (50 per cent lead), **pewter** (25 per cent lead), and **britannia metal** (10 per cent antimony and some copper), are much used in the arts. On account of the action of soft water containing dissolved oxygen on lead (see p. 830), tin pipes are preferred for distributing distilled water and beverages.

Tin is sufficiently valuable to render the **detinning** of scrap tin-plate from can factories, bearing 3 to 5 per cent of tin, a paying process. In the Goldschmidt process the scrap is cleaned, dried, and exposed to dry chlorine, which converts the tin into the liquid stannic chloride $SnCl_4$, but leaves the iron unaffected. The chloride is used in mordanting (p. 825).

Stannous Chloride $SnCl_2,2H_2O$. — This salt is made by the interaction of tin and hydrochloric acid. When the colorless crystals are heated, or when a concentrated aqueous solution is diluted, the salt is partially hydrolyzed. In the latter case the basic chloride $Sn(OH)Cl$ is deposited. By presence of excess of hydrochloric acid, the hydrolysis is prevented. The solution is used as a mordant (p. 648).

Stannous chloride tends to pass into stannic chloride $SnCl_4$, and is therefore an active reducing agent. Thus, it reduces the chlorides of mercury (p. 798) and of the noble metals, liberating the free metals. The action is of the form $Hg^{++} + Sn^{++} \rightarrow Hg + Sn^{++++}$. Stannous chloride reduces cupric and ferric chlorides to the cuprous and ferrous conditions in like manner, *e.g.*:

$$2Fe^{+++} + Sn^{++} \rightarrow 2Fe^{++} + Sn^{++++}.$$

When stannous chloride solution is added to a solution of sodium chloraurate $Na.AuCl_4$, the former reduces the latter, and metallic gold is liberated. The stannic chloride which is formed:

$$2Na.AuCl_4 + 3SnCl_2 \rightarrow 2NaCl + 2Au\downarrow + 3SnCl_4,$$

is hydrolyzed by the water (see below), and the colloidal stannic acid is precipitated, with colloidal gold finely dispersed upon it. The

strongly colored precipitate is called **purple of Cassius,** and is obtained with different tints, often red, according to the degree of dispersion. It is used for gilding porcelain.

Stannous chloride also reduces free oxygen, or, what is the same thing, is oxidized by the air. In this case, stannic chloride is formed in an acidified solution and the liquid remains clear; in the neutral solution a precipitate of the basic chloride is formed as well:

$$6SnCl_2 + 2H_2O + O_2 \rightarrow 4Sn(OH)Cl + 2SnCl_4.$$

Powdered tin, if placed in the bottle along with the acid solution, will undo the effects of this action by reducing the stannic salt to the stannous condition once more.

Stannic Chloride $SnCl_4$. — When chlorine in excess acts upon tin, or upon stannous chloride (either solid or dissolved), stannic chloride is formed. The compound is a colorless liquid (b.-p. 114°) which fumes very strongly in moist air, giving hydrochloric acid and stannic acid. It was formerly known, after its discoverer (1605), as *spiritus fumans Libavii.* The aqueous solution, when freshly made, has almost no conductivity, and the compound is therefore very slightly ionized. As hydrolysis proceeds, the conductivity increases, but the hydrochloric acid is the conducting substance. After a time hydrolysis becomes almost complete. The stannic acid which is formed is not precipitated, however, but remains in colloidal suspension:

$$SnCl_4 + 4H_2O \rightleftarrows 4HCl + Sn(OH)_4.$$

The chloride, with small amounts of water, gives crystalline hydrates $SnCl_4,3H_2O$, $SnCl_4,5H_2O$, and $SnCl_4,8H_2O$, of which the second is used as a mordant under the name "oxymuriate" of tin. Complex salts such as ammonium-stannic chloride or "pink-salt" $(NH_4)_2SnCl_6$ are easily made. Pink-salt is used as a mordant on cotton, and gives a red lake with alizarin (p. 649).

Stannic Acid and its Salts. — When a solution of stannic chloride is treated with ammonium hydroxide, a white, gelatinous precipitate is formed. To this the formula H_2SnO_3 is generally assigned:

$$SnCl_4 + 4NH_4OH \rightarrow 4NH_4Cl + H_2SnO_3 + H_2O.$$

The precipitate, however, loses water gradually until the dioxide remains, and neither orthostannic acid H_4SnO_4 nor metastannic acid H_2SnO_3 is obtainable as a definite compound (compare p. 662). When stannic oxide is fused with caustic soda, **sodium metastannate** $Na_2SnO_3,3H_2O$ is formed:

$$SnO_2 + 2NaOH \rightarrow Na_2SnO_3 + H_2O.$$

This compound is used as a mordant under the name of "preparing salt." When its solution is acidified, stannic acid, the actual mordant, is formed by double decomposition. This stannic acid interacts readily with acids and alkalies, and the chloride obtained from it is identical with stannic chloride described above.

Flannelette and other cotton goods are rendered non-inflammable by saturation first with sodium metastannate solution and then, after drying, with ammonium sulphate. The acid is too feeble and too insoluble to form an ammonium salt:

$$Na_2SnO_3 + (NH_4)_2SO_4 \rightarrow Na_2SO_4 + H_2SnO_3 \downarrow + 2NH_3.$$

The sodium sulphate is washed out and the goods, after being dried, contain stannic oxide. The latter cannot afterwards be removed by washing, and the material is permanently fireproof. Silk is also loaded with stannic oxide, to obtain better shades on dyeing, the amount used varying from 25 to 300 per cent or more.

The metastannates of the metals, aside from those of potassium and sodium, like the silicates and carbonates which they much resemble, are all insoluble in water, and may be made by double decomposition.

The product of the action of nitric acid upon tin is a hydrated stannic oxide (or stannic acid) like — but *not* in all respects identical with — the foregoing substances. It does not easily interact with alkalies. By boiling it with caustic soda, however, and then extracting with pure water, a soluble sodium stannate, $Na_2Sn_5O_{11}$, is obtained. It is also very slowly attacked by acids, and the chloride secured from it is not identical with the ordinary chloride. For these reasons it is supposed by some chemists to be a hydrate of a polymer of stannic oxide $(SnO_2)_5,xH_2O$. When *fused* with caustic soda, however, it gives the same metastannate as does the dioxide itself.

The difference between the properties of the two stannic acids was noticed by Berzelius (1811), and was the first case in which identity in composition was found not to be accompanied by identity in properties (see p. 191). For many years it was generally postulated that two definite stannic acids (α- and β-) existed. It now seems to be established, however, that the differences are

due entirely to particle size and amount of adsorbed water. Substances which show all gradations between the two extreme types have been prepared.

The Oxides of Tin. — When stannous oxalate is heated in absence of air, **stannous oxide** remains: $SnC_2O_4 \rightarrow SnO + CO_2 + CO$. It is a black powder which burns in the air, giving the dioxide. The corresponding **hydroxide** $Sn_2O(OH)_2$ is formed by adding sodium carbonate to stannous chloride solution. It is a white powder, easily dehydrated, and interacts with alkalies to give soluble stannites, such as Na_2SnO_2. When the solution is boiled, tin is deposited, and sodium stannate is formed, the behavior resembling that of cuprous oxide when heated with oxygen acids (p. 791). With acids, the hydroxide gives stannous salts.

Stannic oxide SnO_2 is found in nature (p. 822), and may be made in pure form by igniting precipitated stannic acid. When heated, it becomes yellow, but recovers its whiteness when cooled (compare zinc oxide, p. 747). Prepared at a low temperature, it interacts easily with acids, but after strong ignition is affected by them very slowly.

The Sulphides of Tin. — **Stannous sulphide** SnS is obtained as a dark-brown precipitate when hydrogen sulphide is led into a solution of a stannous salt.

Stannic sulphide SnS_2 is formed likewise by precipitation, and is yellow in color. It is made also by heating together tin filings, mercury, sulphur, and ammonium chloride. The mercury and ammonium chloride are ultimately volatilized, and the stannic sulphide remains in the form of yellow, crystalline scales ("mosaic gold" or "bronze powder"). Stannic sulphide loses sulphur when strongly heated, and leaves stannous sulphide. It is not much affected by dilute acids, but interacts with solutions of ammonium sulphide (or sodium sulphide), giving soluble **complex sulphides,** such as **ammonium sulphostannate:**

$$SnS_2 + (NH_4)_2S \rightarrow (NH_4)_2.SnS_3.$$

The corresponding **sodium sulphostannate** is easily crystallized in the form $Na_2SnS_3,2H_2O$. Stannous sulphide is not affected by soluble sulphides, but polysulphides, such as yellow ammonium sulphide, give with it the above mentioned sulphostannates:

$$SnS + (NH_4)_2S + S \rightarrow (NH_4)_2.SnS_3.$$

With acids the sulphostannates * undergo double decomposition, but the free acid $H_2.SnS_3$ thus produced is unstable and breaks up, giving off hydrogen sulphide, and depositing stannic sulphide.

Analytical Reactions of Salts of Tin. — The two ionic forms of tin, Sn^{++} and Sn^{++++}, are both colorless. Their behavior is different. They give a brown and a yellow sulphide, respectively, with hydrogen sulphide. The interaction of these sulphides with yellow ammonium sulphide (see above) distinguishes them from those of cadmium, copper, and other metals whose sulphides are similarly inactive towards dilute acids. The sulphides of arsenic, antimony, and gold, however, behave like those of tin in this respect. The reducing power of stannous-ion Sn^{++} is very characteristic (p. 824). Zinc displaces tin from solutions of its salts. The oxides are reduced by charcoal in the reducing part of the Bunsen flame and the metal is liberated.

Lead Pb

The Chemical Relations of the Element. — Lead is both bivalent and quadrivalent. Its only known hydride, a volatile liquid PbH_4, is exceedingly unstable. The oxides PbO and PbO_2, and the corresponding hydrated oxides, are both basic and acidic. Lead monoxide is a fairly active base, comparable with cupric oxide, and lead dioxide a feeble one. Both are feebly acidic. The salts of bivalent lead, like $Pb(NO_3)_2$, are somewhat hydrolyzed by water, but less so than are those of tin. The tetrachloride and other salts of quadrivalent lead are completely hydrolyzed. The plumbites $Na_2.PbO_2$ and plumbates $Na_2.PbO_3$ are hydrolyzed to a considerable extent. All the compounds in which lead is quadrivalent give up half of the negative radical readily, and are reduced to the bivalent condition. The metal displaces hydrogen with difficulty (see table on p. 313), and is easily displaced by zinc. Lead compounds are all poisonous, and the effects of repeated, very minute doses are cumulative — resulting in "lead colic." For this reason, the manufacture of white lead is forbidden by law in France, and is subject to strict regulation in other countries.

* These and similar compounds are often called thiostannates, orthothioantimonates, etc. The prefix sulpho- gives more euphonious words, however, and is used here for all excepting the thiocyanates and, of course, the thiosulphates.

Occurrence and Metallurgy. — Commercial lead is almost all obtained from **galena** PbS, which crystallizes in cubes and is found in the United States, Spain, and Mexico. This ore often contains considerable amounts of silver sulphide Ag_2S, and it occurs in association with sulphides of arsenic, antimony, zinc, copper, and iron. Other salts of lead are of less common occurrence.

The ore, if rich in lead content, is roasted in a reverberatory furnace (p. 898) until a part has been converted into the oxide PbO and sulphate $PbSO_4$. The air is then shut off, and the temperature raised, so that these products may oxidize the remaining galenite:

$$PbS + 2PbO \rightarrow 3Pb + SO_2 \uparrow$$
$$PbS + PbSO_4 \rightarrow 2Pb + 2SO_2 \uparrow .$$

The melted lead flows out.

Ores poorer in lead are sometimes reduced by heating with scrap iron, or with a mixture of iron ore and coke. The molten ferrous sulphide rises to the top as a matte.

The purification of the lead from the other metals whose sulphides have been reduced at the same time is often troublesome. In Parke's process (p. 805) for the extraction of the silver by means of zinc, the greater part of the foreign metals, with the exception of bismuth, pass into the zinc scum. About 0.5 per cent of zinc remains in the lead, and is oxidized by the action of a jet of steam before the lead is poured in the molds. Lead is refined electrolytically by the **Betts process.** Heavy plates of the crude lead form the anodes, thin sheets of pure lead the cathodes, and a solution of lead fluosilicate $PbSiF_6$ the cell liquid. The operation is similar to that for refining copper (p. 794). Silver, gold, and bismuth are left as a sludge, while Zn, Co, Ni, and Fe go into solution and are not redeposited.

Physical and Chemical Properties. — Metallic lead is gray in color, very soft, and of small tensile strength. Its specific gravity is 11.4, and its melting-point 327.4°. While warm, it is formed by hydraulic pressure into pipes which are used in plumbing and for covering electric cables. On account of its very slow interaction with most substances, sheet lead is used in chemical factories, for example, to line sulphuric-acid chambers. An alloy containing 0.5 per cent of arsenic is used in making small shot and shrapnel bullets. **Type-metal** contains 20–25 per cent of antimony and expands on solidifying, giving a perfect reproduction of the mold. In both cases greater hardness is secured by the addition of the foreign metal. **Solder** contains 50 per cent of tin and, since it remains liquid at a lower temperature than pure lead,

can be applied in the molten state to mend a lead joint without danger of melting the lead itself.

Lead oxidizes very superficially in the air. The final covering is a basic carbonate. Contact with hard waters confers upon lead a similar coating composed of the carbonate and the sulphate. These deposits, being insoluble and strongly adherent, enclose the metal and protect the water from contamination with lead compounds. Pure rainwater, however, since it has no hardness, and contains oxygen in solution, gives the hydroxide $Pb(OH)_2$, which is noticeably soluble. Hence lead pipes can safely be used only with somewhat hard water. When heated in the air, lead gives the monoxide PbO or minium Pb_3O_4, the latter at lower temperatures.

The metal displaces hydrogen from hydrochloric acid slowly. It is hardly affected by cold concentrated sulphuric acid (compare p. 426). Nitric acid attacks it readily, giving lead nitrate and oxides of nitrogen (p. 532).

The total world's production of lead in 1935 was 1,400,000 metric tons. Of this amount, 300,000 tons were produced in the United States. It is the cheapest metal after iron. Its principal uses have been described above. The metal is also employed extensively in **storage batteries** (see p. 853). Its compounds find important applications as **paint ingredients** (p. 834). **Lead tetraethyl** $Pb(C_2H_5)_4$ is added in small quantities to the gasoline used in automobiles as an "anti-knock."

Chlorides and Iodide.—**Lead chloride** $PbCl_2$ is precipitated when a soluble chloride is added to a solution of a bivalent lead salt. It is slightly soluble in water (1.5 parts in 100) at 18°, and much more so at 100°. **Lead iodide** PbI_2 (yellow) is also formed by precipitation. It crystallizes in beautiful scales from solution in hot water.

Lead tetrachloride $PbCl_4$ is a liquid above —15°, and loses chlorine at the ordinary temperature. It is made by passing chlorine into $PbCl_2$ suspended in hydrochloric acid. The solution contains the complex acid H_2PbCl_6. Ammonium chloride is added and ammonium chloroplumbate $(NH_4)_2PbCl_6$, analogous to pink-salt (p. 825), crystallizes out. When this is thrown into cold, concentrated sulphuric acid, an oil, $PbCl_4$, settles to the bottom. The oil fumes in the air, and closely resembles stannic chloride $SnCl_4$. With little water, it slowly deposits $PbCl_2$, and gives off chlorine. With

much water, it is quickly hydrolyzed, and lead dioxide is thrown down:

$$PbCl_4 + 2H_2O \rightarrow PbO_2 + 4HCl.$$

Lead chloride and iodide are both more soluble in acids or salts with a common negative ion than they are in water, and form soluble, but somewhat unstable, complex salts (compare silver chloride, p. 807).

Oxides and Hydroxides. — There are five different oxides of lead, Pb_2O, PbO, Pb_3O_4, Pb_2O_3, and PbO_2. The **suboxide** Pb_2O is a dark-gray powder, formed by gently heating the oxalate. **Lead monoxide** PbO is made by cupellation (p. 805) of lead, and the solidified, crystalline mass of yellowish-red color is sold as **litharge.** The yellow, powdery form is called **massicot,** and may be obtained by heating the nitrate or carbonate. All the other oxides yield this one when they are heated above 600° in the air. Lead monoxide takes up carbon dioxide from the air, and therefore usually contains a basic carbonate. It dissolves in warm sodium hydroxide solution, giving a plumbite $Na_2.PbO_2$; a saturated solution redeposits part of the oxide in crystalline form when it cools. The oxide is used in making glass and enamels, and for preparing salts of lead. With glycerine, it gives a cement for glass or stone.

Lead hydroxide $Pb(OH)_2$ is formed by precipitation. It gives up water in three stages with different aqueous tensions (compare p. 690), the products in the order of decreasing tension being $Pb(OH)_2$, $Pb_2O(OH)_2$, $Pb_3O_2(OH)_2$. These substances, as will be seen, are equivalent in composition to PbO,H_2O, $2PbO,H_2O$, and $3PbO,H_2O$, respectively. The hydroxide is observably soluble in water, and gives a solution with a faintly alkaline reaction. With acids it forms bivalent salts of lead. It interacts also with potassium and sodium hydroxides to form the soluble **plumbites,** like **sodium plumbite** $Na_2.PbO_2$.

Lead monoxide PbO is also called **plumbic oxide,** and the bivalent salts derived from it are frequently referred to as **plumbic salts.** In view, however, of the confusion that would inevitably be introduced by the use of the names stann*ous* chloride $SnCl_2$ and plumb*ic* chloride $PbCl_2$ in the same chapter, this procedure has not been followed here. $PbCl_2$ cannot be called plumb*ous* chloride, since this ending has been pre-empted by derivatives of Pb_2O. To avoid any ambiguity, and since it is the most familiar halide of lead, derived from the most familiar oxide PbO, it is here called simply **lead chloride,** and $Pb(OH)_2$ is called **lead hydroxide.** Similarly, to save any possibility of confusion, $PbCl_4$ is termed **lead tetrachloride.**

Minium, or **red lead,** Pb_3O_4, gives off oxygen when heated:

$$2Pb_3O_4 \rightleftarrows 6PbO + O_2.$$

The dissociation pressure varies with the temperature: 445°, 5 mm.; 500°, 60 mm.; 555°, 183 mm.; 636°, 763 mm. Since the partial pressure of oxygen in the air is 150 mm., the substance decomposes at about 550°. It can be formed in air by reversal of the action represented above, but only below this temperature (compare p. 724). On account of unequal heating during manufacture, commercial red lead is never fully oxidized, and always contains litharge. Conversely, commercial litharge usually contains a little minium.

Minium, when heated with warm, dilute nitric acid, is decomposed, and leaves lead dioxide as an insoluble powder. Two-thirds of the lead is basic and one-third acidic. Minium is therefore lead orthoplumbate (see p. 833):

$$Pb_2.PbO_4 + 4HNO_3 \rightleftarrows 2Pb(NO_3)_2 + H_4PbO_4.$$

The double decomposition as a salt that it thus undergoes is followed by dehydration of the plumbic acid, which is unstable: $H_4PbO_4 \rightarrow PbO_2 + 2H_2O$, and the dioxide remains. Red lead is **used** in making flint glass and, when mixed with oil, gives a red paint which is specially applicable to iron-work (see p. 800).

Lead dioxide PbO_2 may be obtained as described above in the form of a brown powder. Unlike most oxides, it is a conductor of electricity. It is usually made by adding bleaching powder to an alkaline solution of $Pb(OH)_2$:

$$Na_2.PbO_2 + Ca(OCl)Cl + H_2O \rightarrow 2NaOH + CaCl_2 + PbO_2\downarrow.$$

In this action we may regard the free lead hydroxide, formed by hydrolysis of the plumbite, as being oxidized by the bleaching powder. Lead dioxide is an active oxidizing agent. It interacts with, and sets fire to, a stream of hydrogen sulphide, and it liberates chlorine from hydrochloric acid. With acids it gives no hydrogen peroxide, and its graphic formula $O = Pb = O$ indicates that it is **not** a peroxide (p. 369). Lead dioxide interacts with potassium and sodium hydroxides, giving soluble **plumbates.** These are derived from metaplumbic acid. The potassium salt $K_2PbO_3,3H_2O$ is analogous to the metastannate $K_2SnO_3,3H_2O$ (p. 826). A mixture of calcium carbonate and lead monoxide absorbs oxygen when heated

in a stream of air, and the yellowish-red calcium orthoplumbate is formed:

$$4CaCO_3 + 2PbO + O_2 \rightleftarrows 2Ca_2PbO_4 + 4CO_2.$$

The action is reversible, and is at the basis of Kassner's plan for manufacturing oxygen from the air.

Lead Nitrate $Pb(NO_3)_2$. — This salt may be made by treating lead, lead monoxide, or lead carbonate with nitric acid. It forms white, anhydrous octahedra. The nitrate and acetate (see p. 834) are the salts of lead which, because of their solubility, are most commonly used. The solubility of the nitrate is 48 parts in 100 at 10°, and 153 parts at 100°. Since the solubility increases with rise in temperature, the process of solution is accompanied by absorption of heat (p. 285). On account of hydrolysis, the solution is acid in reaction.

Lead Carbonate $PbCO_3$. — This compound is found in nature in rhombic crystals, isomorphous with those of aragonite. It may be formed as a precipitate by adding a soluble bicarbonate to lead nitrate solution. With normal sodium carbonate, a basic carbonate $Pb_3(OH)_2(CO_3)_2$ is deposited. This basic salt is identical with **white lead,** a heavy, white, insoluble, amorphous substance. Mixed with linseed oil, it forms a white paint valued for its "body" or covering power (see Paints, p. 834). Its disadvantage is the darkening, due to formation of the black lead sulphide PbS, which is produced by the hydrogen sulphide in the air (see p. 369). Its poisonous character is also objectionable.

White lead is manufactured in various ways, all of which involve the oxidation of the lead by the air, the formation of a basic acetate by the interaction of vinegar or acetic acid with the oxide, and the subsequent decomposition of the salt by carbon dioxide. The old **Dutch process** for making white lead is still used extensively. Gratings ("buckles") of lead are placed above a little vinegar in small pots. The pots are covered with boards, on which manure or spent tan bark is spread. Other tiers of pots, boards and bark are placed on the first, until the shed is full. Carbon dioxide, warmth and moisture are furnished by the decaying bark or manure. The gratings, by the end of three months, are converted into cakes of white lead. The vapor of acetic acid arising from the vinegar may be regarded as a catalytic agent, since it is used over and over again.

In the **Mild process** melted lead is atomized by a jet of steam,

and the lead dust is beaten with vinegar, air, and carbon dioxide in a vat for about seven days. In the **French process** white lead is precipitated by a stream of carbon dioxide from a *solution* of the basic acetate.

White lead is now also manufactured electrolytically by the **Sperry process,** in which a solution of lead acetate is electrolyzed in a cell with lead anodes and iron cathodes. The product is exceptionally pure and uniform, brilliant white with an extremely fine grain.

Lead Acetate $Pb(CO_2CH_3)_2,3H_2O$. — This salt is made by the action of acetic acid on litharge. It is easily soluble in water, and from the sweet taste of the solution, is named **sugar of lead** (used in medicine). The basic salt $Pb(OH)(CO_2CH_3)$ is formed by boiling a solution of lead acetate with excess of litharge. Unlike most basic salts, this one is soluble in water, and its solution has a faintly alkaline reaction.

Lead Sulphate $PbSO_4$. — The sulphate occurs in nature as **anglesite,** and is isomorphous with heavy spar. Being insoluble in water, it is easily obtained by precipitation. It is slightly soluble in concentrated sulphuric acid (p. 426), and in nitric acid (compare p. 738). It also interacts with concentrated sodium hydroxide solution, on account of the removal of the Pb^{++} ions which are a factor in its solubility product and their passage into the $PbO_2{}^{=}$ anion of sodium plumbite (compare p. 789). Finally, it dissolves easily in ammonium tartrate, since lead enters into the complex anion of the tartrates in the same way as does copper (p. 791). Barium sulphate, which is of the same order of insolubility as lead sulphate, is very slightly affected by nitric acid, but not by sodium hydroxide or by tartrates. The element barium lacks both the characteristics which lead here exhibits.

Lead Sulphide PbS. — Natural lead sulphide (**galena**) is black, and its crystals have a silvery luster. The precipitated salt is black and amorphous. It is more easily attacked by active acids than is mercuric sulphide (see p. 800). Concentrated nitric acid, being an oxidizing agent as well as an acid, interacts with it readily.

Paints. — Lead compounds, as has already been noted, are used very extensively in paints. A paint usually contains three ingredients:

1. The **oil,** which hardens ("dries") to a tough resin, being oxidized by the air, and adheres firmly to the surface being painted.

2. The **body,** a fine powder which makes the paint opaque. Since the powder does not shrink, it also "fills" the paint and prevents the formation of minute pores which otherwise would appear in the oil after drying. White lead is the most common material for the body, but zinc oxide and other substances are also used.

3. Except in the case of white paint, a **pigment** is added. Various oxides, such as minium, colored salts, and lakes (p. 649) are used as coloring matters.

The oil does not "dry" by evaporation but gives a resin by oxidation (see p. 102). Linseed oil and hemp oil are commonly used. They contain glyceryl esters (p. 632) of unsaturated acids, such as that of linoleic acid, $(C_3H_5(CO_2C_{17}H_{31})_3)$. The unsaturated part of the molecule takes up the oxygen. By previously boiling the oil with manganese dioxide and other oxides, it is rendered more active, and "dries" more quickly.

Plumbers use a cement made of minium and linseed oil, in which the former oxidizes the latter, without access of air being necessary, to make joints tight.

Analytical Reactions of Lead Compounds. — Hydrogen sulphide precipitates the black sulphide, even when dilute acids are present. Sulphuric acid throws down the sulphate. Potassium hydroxide gives the white hydroxide, which dissolves in excess to form the plumbite. Potassium chromate or dichromate (p. 877) gives a yellow precipitate of **lead chromate** $PbCrO_4$, which is used as a pigment under the name of "chrome-yellow."

Titanium, Zirconium, Cerium, Thorium

The metals on the left side of the fifth column of the periodic table are all quadrivalent, although compounds in which a lower valence appears are numerous in this family. The first two are feebly base-forming as well as feebly acid-forming; the last two are base-forming exclusively.

Titanium, although still generally ranked with the rare metals, is actually the tenth most abundant element in nature (p. 28). It occurs in rutile TiO_2 (see Fig. 32, p. 65), and in ilmenite $FeTiO_3$. Rutile is now used in large quantities (50,000 tons annually) in the paint industry, and also as a glaze on porcelain. The

metal itself is employed in making special steel and nickel alloys.

Zirconium is found in zircon, the orthosilicate of zirconium $ZrSiO_4$ (see Fig. 20, p. 60). All zirconium ores contain appreciable quantities of **hafnium,** an element which is exceedingly similar to zirconium in all of its chemical relations. The element is named from Copenhagen (Latin, *Hafniæ*), where it was discovered by Costa and Hevesy in 1923. The position of its X-ray spectra (compare Fig. 133, p. 474) established its atomic number as 72, and methods for its fractionation from zirconium have more recently been perfected.

Cerium occurs chiefly in cerite, a complex silicate in which neodymium, praseodymium and lanthanum (p. 767) are also present. The particles of an alloy of cerium (70 per cent) and iron (30 per cent), when torn off by a file, catch fire in the air. This fact is utilized in making **gas-lighters** and cigar-lighters. **Thorium** is found in thorite $ThSiO_4$, but most of the supply comes from monazite sand. The nitrate $Th(NO_3)_4{,}6H_2O$ is used in making Welsbach incandescent mantles (compare p. 589). The element and its compounds are radioactive (see p. 468).

The foundation of the **Welsbach mantle** is woven of ramie grass or artificial silk. This is saturated with a solution of thorium and cerium nitrates in the proportion 99 : 1, and is then molded to the proper shape and dried. By heating in a Bunsen flame, the organic matter is burned, and the nitrates are decomposed:

$$Th(NO_3)_4 \rightarrow ThO_2 + 4NO_2 + O_2.$$

The oxides retain the form of the fabric and, to prevent breakage in handling, the structure is dipped in collodion and dried.

Exercises. — 1. In what order should you place the elements dealt with in this chapter, beginning with least metallic, and ending with the most metallic (pp. 440–1)?

2. Construct equations showing, (*a*) the interaction of tin and concentrated sulphuric acid, (*b*) of water and stannous chloride, (*c*) of oxygen and stannous chloride in acid solution, (*d*) of lead monoxide and acetic acid.

3. Formulate ionic equations to explain why stannic sulphide dissolves in ammonium sulphide solution.

4. What interactions probably occur when lead dioxide liberates chlorine from hydrochloric acid (see p. 240)?

5. How should you set about preparing, (*a*) lead oxalate (insoluble), (*b*) lead chlorate (soluble)?

6. Construct equations for the formation of white lead by the Dutch process, showing, (1) the formation of the basic acetate by the action of oxygen, water, and acid vapor, and (2) the action of carbonic acid on the product.

7. In what respects do tin and lead behave as non-metals? Write equations

to show the action of sodium hydroxide on the following compounds: stannous hydroxide, stannic oxide, lead monoxide, lead dioxide.

8. A block of tin, weighing 100 kg., is exposed to continued cold weather, and is transformed completely into the gray modification. What is the increase in volume (p. 823)?

9. What weight of chlorine would be required per week in a detinning factory, treating 10 metric tons of scrap, averaging 4 per cent Sn, weekly?

10. Given a powder, which you are told is an oxide of lead, how would you proceed to identify it?

11. Solutions of lead nitrate and sodium orthoplumbate, in equivalent quantities, are mixed. What do you observe? Formulate complete equations.

12. How would you prove that PbO_2 was not a peroxide?

13. What is the percentage of lead in (*a*) white lead (p. 833), (*b*) sugar of lead (p. 834)?

14. Why do the workmen in white lead works add a trace of sulphuric acid to the water they drink?

15. Describe in terms of the categories used in connection with the phase rule (p. 725) the system furnished by minium at 500°.

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CHAPTER XLIX

ELECTROMOTIVE CHEMISTRY

In chemical changes involving electrolytes, which liberate energy, the energy can be secured, if special arrangements are made, in the form of electricity. Since the change sets an electric current in motion, the subject is called **electromotive chemistry.** A knowledge of this branch of the science is essential for the proper understanding of many commercial applications of electricity in chemistry, such as electrolytic methods of refining metals, the theory of storage batteries, etc. It also furnishes us with a simple method for measuring chemical affinity in ionic reactions.

Factors and Units of Electrical Energy. — On account of the close relation between electromotive chemistry and ionization, parts of the former subject were anticipated when the latter was discussed (pp. 305–10). These pages should now be re-read attentively. In particular, it must be recalled that **a quantity of electrical energy is expressed by two factors.** One is the **quantity of electricity,** and is measured in **coulombs.** The other is the **electromotive force (E.M.F.)** in the case of a current, or, when a current is not flowing or is not being considered, the **difference in potential,** and is expressed in **volts.** Just as in electrolysis chemically equivalent quantities of elements or ions, in being liberated from solutions of different substances, *use up* equal quantities of electricity (Faraday's law), so in a battery-cell the interaction of chemically equivalent amounts of different sets of substances *produces* equal quantities of electricity. On the other hand, just as different amounts of thermal energy are liberated or absorbed by different chemical reactions (p. 264), so different amounts of electrical energy are used or generated by the complete interaction of chemical equivalents of different sets of substances, and therefore diverse differences in potential are created and **currents of different electromotive force** are produced.

The electrical energy used or produced is expressed by the product of the factors:

No. of coulombs × No. of volts
= Quantity of electrical energy (in **joules**, p. 257).

If we consider the time occupied by either process, and wish to express the rate at which the energy is consumed or produced, we regard 1 coulomb per second (1 **ampere**) as the unit. Hence:

No. of amperes × No. of volts = Joules per sec. = **Watts.**

The kilowatt is 1000 watts. The horsepower is 746 watts.

An illustration will show the meaning of this relation. If a 50-watt incandescent lamp is used on a 110-volt circuit, by substituting these values in the equation we perceive that such a lamp must carry about 0.5 amperes, or one coulomb every two seconds. If, with the *same* voltage, we wanted a lamp to carry more electricity per second, we should have to reduce the resistance of the lamp, say, by shortening the filament, or using a thicker one. Evidently, the number of such lamps required to consume one horsepower would be 746/50, or between 14 and 15 lamps. Again, to decompose one molecular weight of hydrochloric acid (36.468 g.) by electrolysis of a solution kept at normal concentration during the process 96,500 coulombs (p. 309) are required, and a minimum E.M.F. of 1.35 volts (see p. 848). The electrical energy needed is therefore 96,500 × 1.35 = 130,000 joules. If this were to be accomplished by the current from a 110-volt direct-current lighting circuit, passing through a lamp which carried 5 watts when in series with the electrolytic cell, the time required (x seconds) would be given by: 5 joules per sec. × x secs. = 130,000 joules, where $x = 26{,}000$ seconds, or about 7¼ hours.

The factors of electrical energy (volts and amperes) are easily measured when electricity is produced, and are easily provided according to any specification when electricity is to be used. Hence, it is much easier to study the relations between chemical change and this form of energy than between the same change and the heat or any other form of energy which, under other conditions, it might produce. Electrochemistry is, therefore, in many ways better understood, and easier to handle than are other branches of chemistry involving energy.

Some Reactions That Can Be Used to Furnish Electricity. — A few illustrations of the kinds of reactions which can easily be carried out in cells, so as to furnish electric current instead of heat, may be classified thus:

Combination cells, such as one in which zinc (or some other active metal) and bromine (or some other active non-metal) are the reacting substances:

$$Zn^{0} + Br_2^{0} \rightarrow Zn^{++} + 2Br^{-}.$$

Displacement cells, such as one with cupric sulphate solution and a metal more active than copper (p. 313):

$$Zn^{0} + Cu^{++} \rightarrow Zn^{++} + Cu^{0}.$$

Oxidation cells, such as one in which ferrous chloride $FeCl_2$ or stannous chloride $SnCl_2$ is oxidized by chlorine-water, giving $FeCl_3$ or $SnCl_4$:

$$Sn^{++} + Cl_2^{0} \rightarrow Sn^{++++} + 2Cl^{-}.$$

Concentration cells, or cells in which the same substance, such as silver nitrate, in two different concentrations is used.

On closer analysis, as we shall see below, all of these reactions reduce to the same type — **oxidation** (or **loss of electrons,** see pp. 377–80) at one electrode, and **reduction** (or **gain of electrons**) at the other.

Oxidation-reduction, indeed, includes (for polar compounds, at least), **three of the four main varieties of chemical change** (p. 232) — combination, decomposition, and displacement. In a typical **combination,** such as the combination of iron and sulphur to form ferrous sulphide (p. 22), we have really the two reactions:

$$Fe^{\circ} \rightarrow Fe^{++} + 2\ominus$$
$$S^{\circ} + 2\ominus \rightarrow S^{=}$$

expressed in the single equation: $Fe + S \rightarrow FeS$. **Decomposition,** evidently, is just a reversal of two such reactions. **Displacement** has already been analyzed (p. 313). Only in *double decompositions* do we have no valence changes, and consequently no oxidation-reduction reactions.

It is possible, therefore (and, in a great many cases, very useful) to consider the great majority of chemical reactions as oxidation-reduction phenomena, and to dissect each system into two parts in order to examine the oxidation and the reduction separately. True, we do not ordinarily find it convenient in practice to carry out our processes electrochemically. Most of the oxidation-reduction reactions which have been studied in this volume are of service to chemists, either on a small scale in the laboratory or on a large scale in industry, as methods of preparation, not as sources of electrical energy. Even when we are more concerned with the energy change of a reaction than with its material products, it is often heat or mechanical energy that we desire, not electrical energy. What, then, is the purpose of analyzing reactions in general from an electrochemical view-point?

The answer is: To understand their mechanism more clearly, to discover just where the "driving force" of each reaction is located, to learn how to arrange conditions so as to get the best possible yield or the maximum available energy out of any given reaction, and to develop new and still more efficient methods of utilizing and preparing materials of industrial value.

Let us give an analogy. No business man nowadays is satisfied with knowing that his operations indicate a certain net profit (or loss) over a given period. He needs a detailed balance-sheet, by means of which he can examine separately the showing made by each branch of his organization. The figures tell him immediately where any weak points exist, and he will then take counsel upon how to make improvements. He may decide to strengthen the weak department by adding new men, he may reorganize it from top to bottom, he may scrap it altogether and strike out in a different field.

Just so with the chemist. If he runs a reaction in the ordinary way, with all of the substances in direct contact, he gets a certain net yield of material products and of energy (evolved or absorbed). But he is quite in the dark as to the share taken by each of the reacting substances in bringing about the change. *The electrochemical analysis of the reaction furnishes him with his balance-sheet.* He can see at once whether his oxidizing agent is really efficient or not. He can find out what the reducing agent is doing, whether

it is contributing or consuming energy, and exactly to what amount. Then he can think over the situation point by point, and discover whether he can improve his process by using a different concentration of materials, whether there is available a better oxidizing or reducing agent, or whether he ought to abandon the method entirely in favor of another.

The Arrangement of the Cell. — Every cell has one striking characteristic. If the pairs of substances mentioned in the last section are *placed together* they interact and *heat* is produced. There is no way to avoid the action, and the liberation of the energy as heat, if the substances come in contact. **If, therefore, all the energy is to be obtained as electrical energy, the substances must be prevented from coming in contact with one another.** Paradoxical as it may seem, it is easily possible to obtain the electricity, and yet fulfill this essential condition. The plan in all cells is to place the one substance in or around one pole, and the other substance in or around the other pole, and to separate the substances by a porous partition, or some equivalent arrangement.

Suppose that it is the first of the above-mentioned actions that is to be used — the action of zinc and bromine. The **active substances are arranged** as follows: The pole on the left (Fig. 209) is metallic zinc. The solution on the right contains the bromine. The porous partition in the center is permeable by migrating ions, but hinders mechanical mixing of the materials in the two halves of the apparatus, and so prevents direct interaction with liberation of heat.

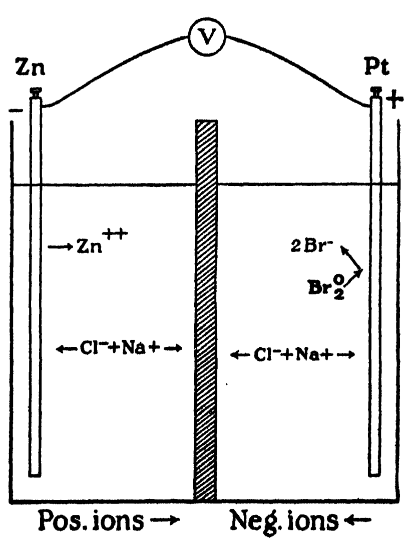


FIG. 209. Combination Cell.

Now, to enable the cell to operate, **inactive, conducting substances must be added** to complete the arrangement. A pole is added on the right, a conducting solution is placed to the left of the partition, and a wire must connect the two poles. The wire may connect the poles through a voltmeter, so that the E.M.F. produced may be measured. Also, since bromine-water is a poor conductor, a well-

ionized salt must be present along with the bromine. The substances used for these purposes must be inactive. For example, the pole on the right must be a conductor, but its material must not interact chemically with the bromine or with the salt. A rod of carbon or a platinum wire will serve the purpose. A more active metal, such as copper, could not be used, because it would combine with the bromine. Again, common salt or sodium nitrate may be mixed with the bromine, because it will not interact with bromine or carbon or platinum. Still again, the solution added on the left must be one which will not act upon the zinc pole, or upon the solution on the right, which it meets inside the porous partition. Common salt or niter fulfills these conditions. An acid could be used on the right, but not on the left, for it would interact with the zinc. The reader should make a different selection of inactive materials, so as to become familiar with the reasoning involved in the choice in each case.

The Operation of the Cell. — When the cell has been assembled, and the wires have been connected, the following phenomena are observed:

1. The zinc, in consequence of its tendency to lose electrons (p. 313), begins to form zinc ions, $Zn^0 \rightarrow Zn^{++} + 2\ominus$, an operation which leaves the pole negative.
2. The bromine molecules which come into collision with the other pole, in consequence of their tendency to gain electrons (p. 359), begin to form bromide ions, $Br_2{}^0 + 2\ominus \rightarrow 2Br^-$, and leave this pole positively charged.
3. Since one pole is now negative and the other positive, a current (stream of electrons, p. 136) flows through the wire.
4. The new positive ions (Zn^{++}) round the left pole attract *all* the negative ions in the cell, and cause them to migrate towards the left so as to keep all parts of the solution electrically neutral.
5. The new negative ions on the right (Br^-) similarly attract *all* the positive ions in the cell, and cause them to drift slowly towards the right pole.
6. (Very important.) It will be seen that the zinc and the bromine **become ionized at a distance from one another and do not actually combine. The chemical change which produces the current is the ionization of the two elements, separately.**

The alternative form of cell shown in Fig. 210 will make this fact clearer to the student. The zinc and platinum poles are immersed in their respective

solutions *in different vessels,* which are connected only by means of an inverted **U**-tube containing salt or niter solution (a "salt bridge"). This bridge can be as long as the experimenter chooses to make it — or there may be, indeed, several successive bridges. The only effect will be to increase the resistance of the circuit and to cut down the quantity of current carried in a given time; the electromotive force of the circuit remains exactly the same.

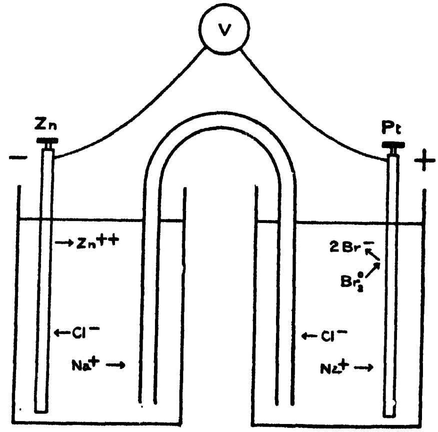


FIG. 210. Alternative Form of Combination Cell.

A Displacement Cell. — In a similar way, a cell using metallic zinc and cupric sulphate solution may be arranged (Fig. 211). The zinc forms one pole, and the cupric sulphate solution *must be placed on the other side* of the partition. For inactive materials, a plate of copper or of some metal below copper in the activity series may be used, and any solution (such as zinc chloride solution) which will interact neither with the zinc nor with the cupric sulphate.

The operation of the cell is substantially as in the previous example. Thus, the zinc begins to lose electrons and gives zinc ion $Zn^0 \rightarrow Zn^{++} + 2\Theta$. The pole on the left becomes negatively charged. The cupric ions which collide with the pole on the right tend to discharge, and consequently begin to gain electrons $Cu^{++} + 2\Theta \rightarrow Cu^0$, leaving the pole positively charged. All the positive ions in the cell migrate towards the right pole and all the negative ions migrate towards the left pole, since positive ions are being formed on the left and are disappearing on the right:

$$Zn^0 + Cu^{++} \rightarrow Zn^{++} + Cu^0 + \text{Electrical energy.}$$

The Oxidation Cell. — The arrangement whereby stannous-ion Sn^{++} is oxidized by chlorine-water to stannic-ion Sn^{++++} is

shown in Fig. 212. The chlorine Cl_2^0 encountering the pole on the right gains electrons and becomes negatively charged, leaving the pole positive. Transfer of electrons takes place along the whole conducting wire (see p. 680). The source of these electrons is the reaction which takes place when stannous ions Sn^{++} touch the

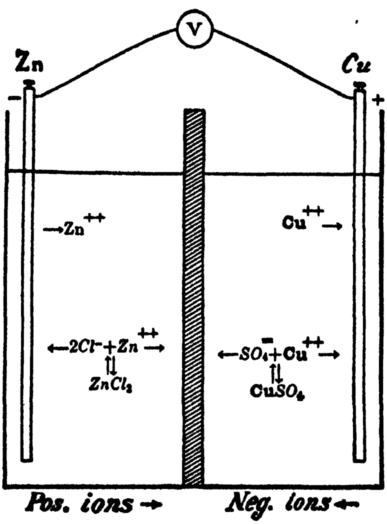


FIG. 211. Displacement Cell.

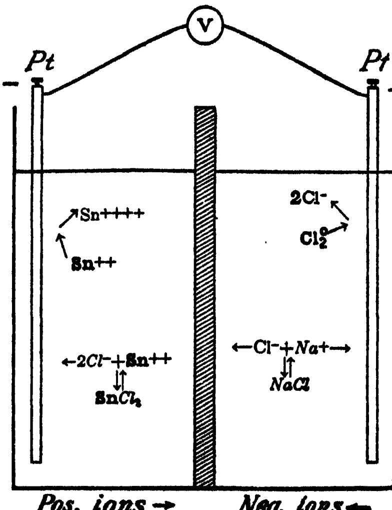


FIG. 212. Oxidation Cell.

electrode on the left: $Sn^{++} \rightarrow Sn^{++++} + 2\ominus$. The complete reaction is therefore:

$$Sn^{++} + Cl_2^0 \rightarrow Sn^{++++} + 2Cl^- + \text{Electrical energy.}$$

A rather more complex example of an oxidation cell is obtained when we introduce hydrochloric acid on the one side of our apparatus and a solution of potassium permanganate on the other. The reaction which occurs in this case:

$$2MnO_4^- + 16H^+ + 10Cl^- \rightarrow 2Mn^{++} + 8H_2O + 5Cl_2^0$$

may thus also be utilized as a source of electrical energy. The student should refer back, at this point, to the detailed discussion given to this reaction in an earlier chapter (pp. 379–80).

Facts Concerning All Cells. — If the wire is disconnected, the progress of the oxidation and reduction reactions at the respective electrodes automatically stops. The charge conferred upon a pole must be conducted away, before additional charges will be transferred to it.

If a glass partition is substituted for a porous one, the cell ceases to generate electricity. The partition must permit the trans-migration of the ions, which is a necessary part of the operation of the cell.

When the circuit is closed, the changes described go on until one of the active materials is practically exhausted — for example, until practically all the cupric-ion has been deposited as copper, or until practically all the zinc has been consumed.

The quantity of electricity produced is 96,500 coulombs for each equivalent weight of the active materials transformed, *e.g.*, for every 65.37/2 g. of zinc consumed. The *rate* at which the electricity is produced is, in general, greater the larger the area of the poles. The amperage of a *single* cell is, in general, very low.

The E.M.F. of the cell is not changed by altering the size or shape of the poles, or by using more or less of the solutions. It *is* affected by any change in the *qualities* of the *active* materials, however. Changing the concentration of the cupric-ion (Fig. 211) or of the bromine-water (Fig. 209) has an immediate effect. So has substituting one active metal for another, as magnesium for zinc (Fig. 209). The reasons for such differences may now be developed.

Single Potential Differences Produced by the Metals. — It will be evident, from the discussion on the operation of the cells given above, that there are really **two chemical actions in each cell** and that these are concurrent and independent. We can leave the zinc (Fig. 209) constant, and change the concentration of the bromine or even substitute chlorine or iodine for the latter. The reaction: $Zn^0 \rightarrow Zn^{++} + 2\ominus$ at the negative pole is unaffected. On the other hand, we can leave the bromine-water constant, and exchange the zinc for some other active metal, without disturbing the reaction: $Br_2^0 + 2\ominus \rightarrow 2Br^-$ at the positive pole. Thus, the E.M.F. of every cell is really the resultant of two effects. Now these effects can be considered separately.

If we place a stick of metallic zinc in a solution of zinc chloride, we find that there is at once a difference in potential between the metal and the solution. The atoms of the metal have an individual tendency to assume the ionic state or, in other words, to give up electrons (p. 313): $Zn^0 \rightarrow Zn^{++} + 2\ominus$. On the other hand, the Zn^{++} ions already in the solution have a tendency to take up electrons and become neutral, according to the reverse equation: $Zn^{++} + 2\ominus \rightarrow Zn^0$. If the former tendency (the tendency to give up electrons) is the stronger of the two (as it is, for solutions of

ordinary concentration, with the more active metals), then a difference in potential is produced, with the solution positive with respect to the metal. If the latter tendency is the stronger (as it is, for solutions of ordinary concentration, with the less active metals) the solution is observed to be negative with respect to the metal. Raising the concentration of the metal-ions will increase the tendency to deposition and *vice versa,* while the tendency of the metal to form metal-ions is constant (compare, very carefully, the discussion on solution equilibria, p. 218). It is customary, therefore, always to take as the standard solution, in comparing potential differences, one in which the concentration of the metal-ions is normal (N). It is also customary, in consequence of the impossibility of determining absolute electrode potentials accurately, to assume the potential of a platinum electrode saturated with hydrogen gas under 1 atmosphere pressure against a solution normal with respect to hydrogen-ion as zero, and to refer all other potentials to this as a standard. This does not mean that the reaction: H_2 (at 1 atm.) $\rightarrow 2H^+$ (in N solution) $+ 2\ominus$ involves no gain or loss of electrical energy, but only that the potentials of other elements against normal concentrations of their ions differ from that of hydrogen by the values given. In the following table, the sign preceding the number is the charge of the free metal. It will be seen that the most *electropositive* metals acquire the highest *negative* potential, in consequence of their extreme tendency to throw off *positively charged ions, e.g.:* $K \rightarrow K^+ + \ominus$.

POTENTIALS OF METALS IN CONTACT WITH N SOLUTIONS
(ELECTROMOTIVE SERIES)

Li	−3.02	Cr (Cr^{++})	−0.6(?)	Sb	+0.1(?)
K	−2.92	Cr (Cr^{+++})	−0.5(?)	Bi	+0.2(?)
Na	−2.72	Fe (Fe^{++})	−0.43	As	+0.3(?)
Ba	−2.8(?)	Cd	−0.40	Cu (Cu^{++})	+0.34
Ca	−2.5(?)	Ni (Ni^{++})	−0.22	Cu (Cu^+)	+0.51
Mg	−1.55	Sn (Sn^{++})	−0.14	Hg (Hg^+)	+0.79
Al	−1.34	Pb (Pb^{++})	−0.13	Ag	+0.80
Mn (Mn^{++})	−1.0(?)	Fe (Fe^{+++})	−0.04	Hg (Hg^{++})	+0.86
Zn	−0.76	H_2	0.00	Au (Au^+)	+1.5(?)

The "normal potentials" of some non-metallic elements, and of some typical oxidation-reduction reactions, may also be appended:

F_2	+1.9(?)	$O_2 + 2H_2O + 4\ominus \rightarrow 4OH^-$	+0.40
Cl_2	+1.35	$MnO_4^- + 8H^+ + 5\ominus \rightarrow Mn^{++} + 4H_2O$	+1.52
Br_2	+1.08	$Pb + SO_4^{=} \rightarrow PbSO_4 + 2\ominus$	−0.34
I_2	+0.62	$PbO_2 + 2H^+ + 2\ominus \rightarrow H_2O + PbO$	+1.66

Applications: E.M.F. of a Displacement Cell. — For a cell in which one metal is going into solution and another is being deposited — like that with zinc and cupric sulphate — we can calculate from the foregoing data the E.M.F. of the cell. Metallic zinc, in contact with normal zinc-ion solution, is listed with a *negative* potential of 0.76 volt. Metallic copper, in contact with normal cupric-ion solution, is listed with a *positive* potential of 0.34 volt. The potential difference between the two electrodes is consequently the algebraic difference of these values, *i.e.*, 1.10 volts.

The Daniell or **gravity cell** (Fig. 213) makes use of the above facts. The copper plate is at the bottom and the zinc is suspended above it. The cell is filled with dilute sodium chloride solution and crystals of cupric sulphate are thrown in. So long as the cell is not disturbed, the heavy, saturated solution of cupric sulphate remains at the bottom, so that no porous partition is required. It is true that, when the current is not being used, and the cell is not working, the cupric sulphate diffuses upwards. During the time that the circuit is closed, however, the effects of diffusion are nullified by the migration of the cupric-ion away from the zinc and towards the positive pole. The actual E.M.F. of this cell is not exactly that calculated above for normal solutions, because the cupric sulphate is in saturated solution, and the concentration of the zinc-ion varies, starting at zero and increasing as the cell is used. It is, however, a little over 1 volt.

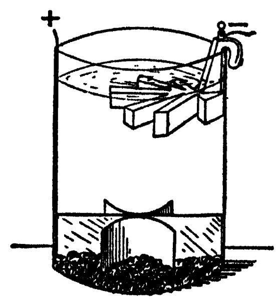


FIG. 213. Daniell Cell.

The cell **zinc-hydrogen** (Fig. 104, p. 254), which furnishes 0.76 volt (theoretically) at normal ionic concentrations, also works without a porous partition, provided the direct action of the zinc on the acid is minimized by adequate amalgamation with mercury. It gives a very inconstant electromotive force, however, because the platinum plate used as the positive pole becomes covered with bubbles of hydrogen, and so the internal resistance of the cell is greatly increased. The polarization (p. 310) also diminishes the electromotive force. These difficulties are remedied, and, in fact, a great increase in the E.M.F. of the cell is effected, by surrounding the positive pole with an oxidizing agent which shall convert the hydrogen into water. The energy obtainable is thus that of a strong oxidizing agent on zinc, and not merely that of an acid. In the

Bunsen cell the positive pole is a carbon block surrounded by concentrated nitric acid. In the **dichromate battery** it is a carbon block with chromic acid. Each of these cells gives an E.M.F. of 1.9 volts. In the **Leclanché cell** the positive pole is a mixture of carbon and manganese dioxide, and the fluid is a solution of ammonium chloride from which the zinc displaces hydrogen. The dioxide, being solid, oxidizes the hydrogen slowly, and the cell can be used for only a few minutes at a time without becoming polarized. The E.M.F. is 1.48 volts. **Dry cells** are of the same nature, but contain a porous solid (*e.g.* kieselguhr, p. 660) which holds the liquid by capillary forces (for Accumulators, see p. 853).

A cell is thus an engine for the direct transformation of chemical into electrical energy, just as a steam-engine transforms chemical energy, by several stages, it is true, into mechanical energy. The cell is driven by potential differences in the materials in and around the two poles.

The **Weston Standard Cell** contains a pole of mercury in a saturated solution of mercurous sulphate, and a pole of cadmium in contact with saturated cadmium sulphate solution. For normal ionic concentrations, the voltage of such a combination would be $0.79 + 0.40 = 1.19$ volts. At 20° the Weston cell, as actually set up, possesses 1.0183 volts.

The **Clark Standard Cell** contains zinc and zinc sulphate solution in place of the cadmium. With normal ionic concentrations this combination would give $0.79 + 0.76 = 1.55$ volts. With saturated solutions, as used in practice, it gives 1.434 volts.

Electrolysis: Decomposition Potentials. — When a solution of cupric chloride is electrolyzed, copper and chlorine are liberated at the two poles. Now, when the electrolysis has made some progress, if the battery is taken out, and the wires are joined, a reverse current, the **polarization current** (p. 310), is found to flow. Evidently, the copper and chlorine liberated in and around the electrodes have made the arrangement into a copper-chlorine battery cell. Assuming normal ionic concentrations, the E.M.F. of the polarization current is $1.35 - 0.34 = 1.01$ volts. Now this counter-e.m.f. is in operation during the whole electrolysis. To overcome it, and maintain the electrolysis, evidently an E.M.F. of at least 1.01 volts from the battery is required. This is called the **decomposition potential** for cupric chloride. The decomposition potentials of other electrolytes in solutions of normal ionic concentration may be calculated by the student from the tables given on p. 846.

Electrolytic Refining. — The electrolytic process for refining copper (read p. 794) can now be more easily understood. *Both* electrodes are made of copper, and the solution contains cupric

sulphate. There is, therefore, no difference in potential between the plates, except a very small one, due to the fact that one plate is pure copper and the other impure. Hence a very slight E.M.F., sufficient to overcome the difference just mentioned, and to move the ions at a suitable speed between the electrodes (see p. 315), is all that is required, and with a high amperage less than 0.5 volt is sufficient.

As regards the resulting **purification,** the anode of crude copper, which is being consumed, contains, besides copper, small amounts of less active metals like silver and gold, and of more active metals like zinc. So far as the more active metals are concerned, the cell is like one with zinc and cupric sulphate (p. 847). It would run *by itself* without any outside current, and would actually generate a current. Hence the active metals easily become ionic, and displace cupric-ion from the solution. The less active metals, on the other hand, require a larger E.M.F. for their ionization than is being supplied. Hence they remain as metals, and drop to the bottom of the cell (sludge) as the anode of crude copper wears away.

Couples. — We have noted (pp. 132, 254) that contact with a platinum wire, or the presence of impurities (other metals) in zinc, will hasten its action upon an acid. Pieces of two metals in contact with one another constitute a **couple.** With zinc and platinum in an acid, a current is set up, like that of a short-circuited cell. The zinc becomes negative, the platinum positive, and the hydrogen is *liberated upon the platinum.* This facilitates the action because, when the platinum is absent, and the hydrogen gas, in bubbles, is liberated on the surface of the zinc, this surface is only partly in contact with the acid (H^+), and so the liberation of the hydrogen is slower.

Galvanized iron is also a couple. When rain (dilute carbonic acid) falls upon it, the zinc, being the more active metal (p. 846), tends to become ionized (giving the insoluble carbonate) and forms the negative electrode. The iron, which is not affected so readily, becomes the positive electrode and is consequently inert. The carbonate, however, forms a closely-adhering coating upon the zinc, and so but little of this metal is actually consumed, and the material is therefore durable. On the other hand, a sheet of iron, without the zinc coating, gives ferrous carbonate which is easily oxidized to ferric hydroxide (a base too weak to give a carbonate). This forms a brittle, porous layer which does not mechanically

protect the surface from further action, and so the iron is finally all oxidized. **Tin-plate** (tin on iron, a couple) is not attacked so long as the layer of tin is nowhere broken. But damaged tin-plate rusts rapidly. There, the iron is the more active metal (p. 846) and forms carbonate and then hydroxide continuously, while the tin remains unaffected.

Rusting. — It seems to be generally overlooked that *two* factors are concerned in determining the **extent to which the rusting** or tarnishing **of a metal will proceed.** Other things being equal, it should depend upon the order of activity of the metals, since it is a question of action upon surface moisture containing carbonic acid, with atmospheric oxygen as an assistant when the metal does not liberate elementary hydrogen (*e.g.*, Copper, p. 785). But this applies only to the initiation of the action. The physical qualities of the product then determine whether the rusting shall be superficial or shall go deeper. Magnesium (p. 742) and iron (p. 904) give carbonates, and the latter eventually a brittle, scaly hydrated oxide. In both cases, the porous product harbors moisture and thus promotes further rusting. Aluminium is more active than is iron, but the horny, gelatinous, closely adherent hydroxide first formed protects the surface from further action. The same is true of zinc and tin.

Concentration Cells. — If two rods of a metal (*e.g.*, silver) are placed together in the same solution of a salt of the metal (*e.g.*, silver nitrate, $AgNO_3$), there is no difference in potential, because the state of both poles is in all respects the same. But if the solution round one pole is more concentrated than that round the other, a difference in potential is produced. The tendencies of the metallic silver to form ions are equal, but the tendencies of argentic-ion to deposit upon the electrodes are different (see p. 846), and so when the circuit is closed, silver ions are discharged on the silver pole in the more concentrated solution, forming long crystals of silver, and silver in equal amount from the pole in the dilute solution becomes ionic.

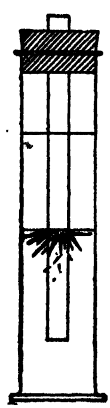


FIG. 214. Tin Concentration Cell.

Figure 214 shows a simple lecture illustration, where a concentrated, denser solution of stannous chloride $SnCl_2$ is below, and a more dilute solution of less density above, and one rod of tin, passing through both layers, furnishes at once the two poles and the connection. Chloride-ion migrates through the solution, in a direction opposite to that taken by the tin ions, and thus passes upwards into the dilute solution to balance the

fresh tin ions that are continuously formed. All change ceases when the concentrations have become equalized.

It has been demonstrated that, for univalent ions, a *ten-fold difference of ionic concentrations* around the two electrodes at ordinary temperatures results in an E.M.F. of nearly 0.06 volt. A hundred-fold difference gives 0.12 volt, a thousand-fold 0.18 volt, and so on. For bivalent ions, the corresponding electromotive forces produced are one-half the above values; for trivalent ions, one-third. It is possible, therefore, to use the concentration cell for **measuring solubilities of insoluble salts.** Thus, we cannot easily measure the solubility of silver chloride by the ordinary method (p. 200), because evaporation of the solution may leave a larger mass of impurities, derived from solution of the glass, than of dissolved silver chloride. Hence, we use two poles of silver, place one in normal silver nitrate solution and the other in saturated silver chloride solution (with excess of the solid), measure the difference in potential, and calculate the ratio of the concentrations of silver-ion in the two solutions.

The concentration cell is instructive because it shows that the order of the metals in the electromotive series is not determined by the metal alone, but also by the concentration of the solution. The order of the metals in the electromotive series is therefore subject to variation. An extreme case of this occurred in a recent chapter. Zinc displaces copper from a solution of a cupric (or cuprous) salt, and any but a prodigiously dilute solution will show the effect. But a solution containing cuprocyanide-ion $Cu(CN)_2^-$ has precisely the very minute concentration of copper ions which will turn the scale. Hence, zinc will not displace copper from this solution (p. 792). On the contrary, copper will displace zinc from a solution of a salt of the latter containing excess of potassium cyanide!

This concentration factor is of such importance that it will be worth while to reconsider the above case to appreciate its significance more fully.

Suppose we take the displacement cell illustrated in Fig. 211, and arrange matters at the start so that the concentrations of Zn^{++} in the zinc chloride solution and of Cu^{++} in the copper sulphate solution are both normal (1 g. equiv. per liter). We note that the voltmeter, when the zinc and copper plates are connected, registers an E.M.F. for the cell of $0.76 + 0.34 = 1.10$ volts, and that the passage of the current involves deposition of copper on the positive pole and formation of zinc ions around the negative pole.

But now suppose we reduce the concentration of Cu^{++} *progressively*, while keeping the concentration of Zn^{++} normal, by adding in different experiments (*a*) sodium hydroxide, (*b*) ammonium hydroxide, (*c*) hydrogen sulphide, and (*d*) potassium cyanide in excess to the copper sulphate solution. The less Cu^{++}

there is present in this solution, the harder it becomes to discharge it (p. 846). Quantitatively, the discharge potential for this bivalent ion increases nearly 0.03 volt for each tenfold decrease in concentration, and the E.M.F. of the cell will be reduced accordingly.

Now, by addition of sodium hydroxide, we lower the concentration of Cu^{++} to the value required by the solubility product of cupric hydroxide. This, however, is not an exceedingly insoluble substance, and the change in the voltmeter is not significant. Addition of ammonium hydroxide reduces the concentration of Cu^{++} further, to the value corresponding to the *instability constant* of $Cu(NH_3)_4^{++}$, but still the falling-off in the E.M.F. of the cell is small. Copper sulphide is so exceedingly insoluble that addition of H_2S does involve a very marked drop in the voltage, but it is only when potassium cyanide is added in excess that we find that the concentration of Cu^{++} has been so prodigiously reduced, owing to the fact that the complex ion $Cu(Cn)_3^-$ is so phenomenally stable, that *the current is now flowing in the opposite direction.* Zn^{++}, *in normal concentration,* has actually a lower discharge potential than Cu^{++} *in the extremely minute concentration in which it now exists* in the solution. The copper plate has become the negative pole and is furnishing Cu^{++}; the zinc plate has become the positive pole and metallic zinc is being deposited upon it.

By manipulating concentration ratios, or by using complex ions and such-like devices, we are consequently able to arrange matters so as to force whichever constituent we wish out of a solution, or to drive any substance we wish into a solution. A great number of technical processes are founded upon this principle.

A Lecture Demonstration. — A striking illustration as to how the concentration factor influences the course of an electrolysis may be obtained by electrolyzing various solutions of sodium chloride, introducing resistances into the circuit so that the potential drop between the electrodes in each case is not very much above the minimum decomposition potential (p. 848). Under such circumstances, a very dilute solution gives practically pure oxygen at the anode. As the salt content is progressively increased, chlorine appears admixed with oxygen in larger and larger proportions. A concentrated solution gives practically pure chlorine. At the cathode, hydrogen alone is evolved, whatever the concentration.

How can these results be explained? Consider first the phenomena at the cathode. If the only ions present are Na^+ and Cl^-, why is hydrogen liberated instead of sodium? The old explanation was that Na^+ was discharged at the electrode and that the free metal immediately reacted with the water to give NaOH and H_2. This explanation cannot be sustained in the light of the preceding paragraphs. Although the concentration of H^+ in a solution of sodium chloride is relatively minute (about 1×10^{-7} N; just as in pure water) yet even at much lower concentrations than this the discharge potential of H^+ would still be considerably below that of normal Na^+, as may be seen from the table on p. 846. The Na^+ congregates around the cathode, therefore, but is never discharged at all, under ordinary conditions.

Can we ever force Na^+ out of the solution? Yes, by using a voltage much greater than the minimum, a high current density and a mercury cathode. Under these conditions, an amalgam (p. 695) is formed at the cathode, which contains very little free sodium, the greater part of the metal being combined chemically with the mercury. This constitutes the basis of the Castner-Kellner method for the manufacture of sodium and potassium hydroxides (p. 700).

How about the anode phenomena? From the second table on p. 846 we derive the following values:

$$Cl_2 + 2\ominus \rightarrow 2Cl^- \qquad +1.35 \text{ volts}$$
$$O_2 + 4H_2O + 4\ominus \rightarrow 4OH^- \qquad +0.40 \text{ volt}$$

It is consequently much easier for OH^- to lose an electron than for Cl^-; the discharge potentials for normal solutions differ by nearly a volt. If, therefore, the initial concentrations of *both ions* are small (as in a very dilute solution of NaCl) we shall obtain practically pure oxygen on electrolysis. But if we increase the concentration of Cl^-, we soon reach a point where (especially after the current has passed for a time) it becomes just about as easy to discharge Cl^- as to discharge OH^-. We therefore obtain chlorine admixed with oxygen at the anode, and the proportion increases until, with concentrated NaCl solution, practically pure chlorine is evolved.

Solutions of oxygen acids like sulphuric acid show a trace of decomposition at about 1.2 volts, due to the H^+ and OH^- present therein. But it is only when the E.M.F. reaches the decomposition values for H^+ and $SO_4^=$, and H^+ and HSO_4^-, namely, 1.96 and 2.66 volts, that rapid electrolysis begins. This observation answers, incidentally, the question whether in the so-called "electrolysis of water," when dilute sulphuric acid is used, it is the water or the acid that is decomposed. The H^+ and OH^- decomposition at 1.2 volts is very slight, because of the exceedingly small concentration of the OH^- in the acid solution (about 1×10^{-14} N in normal acid), and a lens is required for its recognition. The more vigorous action resulting from the discharge of $SO_4^=$ and HSO_4^- by the use of 2–3 volts is therefore the one invariably used.

In view of the foregoing facts, it is probably most correct to say that when dilute sulphuric acid is electrolyzed, *e.g.*, as a lecture experiment, the oxygen liberated at the anode comes mainly from a secondary interaction of the discharged material of the anions with the water (p. 308). A minute proportion of the oxygen in such an experiment does arise from primary electrolysis of the water, but this effect of the current is in itself too slight to be visible at a distance. When, on the other hand, the solution electrolyzed contains a salt of sodium, and hydrogen is liberated at the cathode, this gas may be regarded as coming essentially from primary electrolysis of the water. With a very high E.M.F. and sufficient current density, however, sodium-ion is doubtless actually discharged (see above), and in that case a part of the hydrogen liberated is furnished by the interaction of the metal with the water.

The Storage Battery. — In the ordinary **lead accumulator** the plates consist of leaden gratings. The openings in these gratings are filled with finely divided lead in one plate and with lead dioxide in the other. These, and the dilute sulphuric acid in the cell, are the active substances when the cell is charged. When the battery

is used as a source of current, the $SO_4^=$ ions migrate towards the platc filled with the lead (Fig. 215), and convert this lead into a mass of the insoluble lead sulphate: $SO_4^= + Pb \rightarrow PbSO_4 + 2\Theta$. This plate, therefore, becomes negatively charged. Simultaneously, the H^+ ions move towards the other plate and there reduce to monoxide the lead dioxide with which it is filled:

$$PbO_2 + 2H^+ + 2\Theta \rightarrow H_2O + PbO.$$

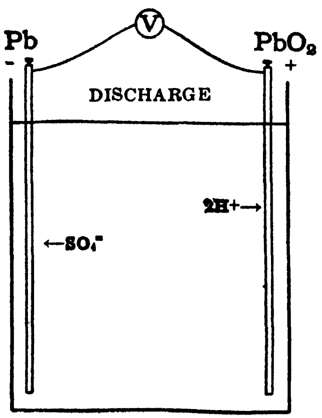


FIG. 215. Lead Accumulator in Use.

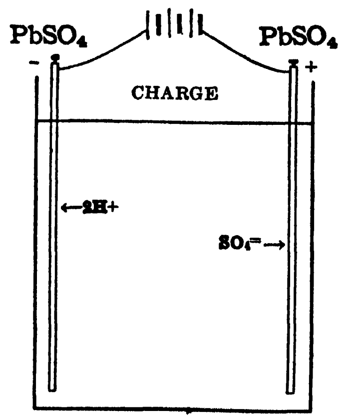


FIG. 216. Lead Accumulator Recharging.

This plate consequently becomes positively charged and, by interaction of the lead monoxide with the sulphuric acid, becomes filled, like the negative plate, with lead sulphate. During the discharge, much sulphuric acid is thus removed from the cell fluid, and the approaching exhaustion of the cells can therefore be ascertained by measuring the specific gravity of the fluid. The E.M.F. of the current is a little over 2 volts (for *normal* ionic concentrations it would be $0.34 + 1.66$, or *exactly* 2 volts, see table on p. 846).

The cell may be **recharged** by passing a high-voltage current through the cell, in the opposite direction (Fig. 216).

In the **Edison cell,** when charged, one plate is of iron and the other contains nickel dioxide NiO_2. The cell liquid is a solution of potassium hydroxide When the cell operates, the nickel dioxide is reduced to $Ni(OH)_2$ and the iron is oxidized to $Fe(OH)_2$, an action which delivers energy:

$$Fe + 2H_2O + NiO_2 \rightleftarrows Fe(OH_2) + Ni(OH)_2.$$

When the cell is recharged, the nickel is reoxidized and the iron reduced.

Exercises. — 1. Make diagrams of the following cells, choosing with care suitable inactive substances to complete the arrangement: (*a*) chlorine-water and aluminium; (*b*) chlorine-water and ferrous chloride; (*c*) zinc and dilute hydrobromic acid; (*d*) chlorine-water and potassium iodide.

2. Calculate the E.M.F. of each of the above cells, assuming normal solutions to be present.

3. What will be the decomposition potentials of solutions of the following substances, assuming *N* concentrations of the ions: (*a*) manganous chloride; (*b*) hydrogen iodide; (*c*) ferrous bromide; (*e*) sodium chloride (hydrogen is liberated)?

4. What weight of zinc must be ionized every hour in a cell in order to produce a current of 5 amperes strength? For how long would 500 g. of zinc serve to maintain this current?

5. In the zinc-bromine cell (p. 841), why is the zinc pole called the anode, although its charge with respect to the platinum is negative?

6. What will be the effect upon the E.M.F. of the cell shown in Fig. 211 of adding concentrated ammonium hydroxide in excess to the solution: (*a*) on the left-hand side, (*b*) on the right-hand side? Formulate an explanation by means of ionic equations.

7. Make a sketch of a combination cell, using magnesium as one pole and a solution of chlorine around the second pole. What metals could, and what could not, function as the second pole in such a cell? What salts could, and what salts could not, be used to make the solution conducting? Describe the working of the cell in detail. If, after a time, the concentration of Mg^{++} around the first pole was *N*, and the concentration of Cl^- around the second pole was *N*, what would be the E.M.F. of the cell? Is the term "combination cell" strictly accurate?

8. Sketch a displacement cell, using cadmium as one pole and a solution of silver nitrate around the second pole. Proceed now to answer the same questions as in Exercise 7, making the necessary substitutions.

9. Sketch an oxidation cell, using hydrochloric acid around one electrode and a solution of potassium permanganate around the other. Proceed now to answer the same questions as in Exercise 7, making the necessary substitutions

10. Sketch a concentration cell, using normal silver nitrate solution around one electrode and a saturated silver iodide solution (with excess solid) around the other. Proceed now to answer the same questions as in Exercise 7, making the necessary substitutions (see also Exercise 11 below).

11. A saturated solution of silver iodide at 18° is 1×10^{-8} normal. What is the E.M.F. of the concentration cell in Exercise 10?

12. Explain in detail why gold interacts with *aqua regia*, although its normal electrode potential is very much below that of hydrogen.

13. What are the decomposition potentials for solutions of the following substances, assuming *N* concentrations of the ions: (*a*) cadmium bromide, (*b*) hydrobromic acid, (*c*) cadmium iodide, (*d*) nickelous chloride?

14. Why does the addition of a few drops of silver nitrate accelerate the action of dilute sulphuric acid on nickel?

15. Describe in detail how you would determine the solubility of silver bromide in water.

16. What are the reactions which take place (*a*) at the anode, (*b*) at the cathode of the Edison cell? Use the ion and electron method to analyze the equation on p. 855.

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CHAPTER L

ARSENIC, ANTIMONY, BISMUTH

This family is very closely related to the elements phosphorus and nitrogen which precede it in the same column of the periodic table. In reading this chapter, therefore, constant reference should be made to the corresponding compounds of phosphorus.

Each of the three elements, **arsenic** (As, atomic number 33), **antimony** (Sb, at. no. 51), and **bismuth** (Bi, at. no. 83), gives two sets of compounds, in which it is trivalent and quinquivalent respectively. Arsenic is mainly an acid-forming element, and is therefore generally regarded as non-metallic, while antimony is both acid-forming and base-forming, and bismuth is mainly base-forming. None of the elements when free displaces hydrogen from dilute acids.

ARSENIC As

The Chemical Relations of the Element. — Arsenic forms a compound with hydrogen AsH_3 (two other hydrides, As_2H_2 and As_2H_4, have been isolated, but are exceedingly unstable). It gives several halogen derivatives of the type AsX_3, which are hydrolyzed by water. Its only pentahalide is the fluoride AsF_5. Its oxides and hydroxides are predominantly acidic. Sulphates, nitrates, carbonates, and other salts of arsenic are not stable. The complex sulphides are important. The soluble compounds of arsenic are all highly **poisonous.**

In many natural sulphides, such as pyrite FeS_2 and zinc-blende ZnS, a part of the sulphur is replaced by arsenic, which must here be playing the part of a bivalent element.

Occurrence and Preparation. — Arsenic is found free in nature. It occurs also in combination with many metals, particularly in **arsenical pyrite** (mispickel) FeAsS. Two sulphides, **orpiment** As_2S_3 and **realgar** As_2S_2, and **white arsenic** As_2O_3, are less common.

The element is obtained either from the native material or by heating arsenical pyrites: $FeAsS \rightarrow FeS + As$. During the roast-

ing of the sulphur ores of metals, arsenic trioxide is formed by the oxidation of the arsenic so frequently present, and collects as a dust in the flues. By distilling the deposit with carbon, free arsenic is obtained as a crystalline metallic sublimate (**gray arsenic**):

$$As_2O_3 + 3C \rightarrow 2As\uparrow + 3CO\uparrow.$$

Properties and Uses. — The element has a silvery luster, but tarnishes quickly. When it is heated, its vapor reaches a pressure of 760 mm. before the melting-point is attained, so that the metal sublimes (at 615°) without melting.

The density of the vapor measured at 615° gives 308.4 as the weight of the G.M.V. (22.4 liters at 0° and 760 mm.). The weight of arsenic combining with one chemical unit weight (35.46 g.) of chlorine is 25 g. Three times this amount, or 75 g., is the smallest weight found in the G.M.V. of any volatile compound of arsenic, and is therefore accepted as the atomic weight (p. 187). Since 308.4 is equal approximately to 4×75 (= 300), the formula of the vapor of the simple substance at 615° is As_4. At 1700° the formula is As_2 (compare p. 194).

By rapidly cooling arsenic vapor, **yellow arsenic**, an unstable form corresponding to white phosphorus, soluble in carbon disulphide, is obtained. A third modification — **black arsenic** — is also known.

The free element burns in the air, producing clouds of the solid trioxide As_2O_3. It unites directly with the halogens, with sulphur, and with many of the metals. When boiled with nitric acid, chlorine-water, and other powerful oxidizing agents (p. 847), it is oxidized in the same way as is phosphorus, and yields arsenic acid H_3AsO_4.

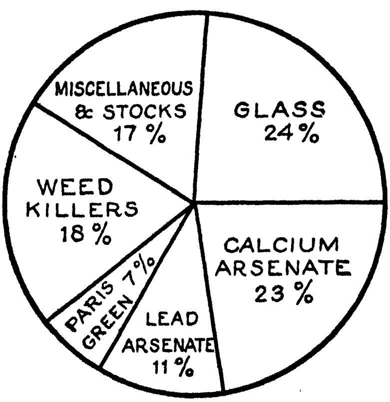


FIG. 217. Distribution of Arsenic in Industry.

In the making of **small shot,** about 0.5 per cent of arsenic is added to the lead. The latter is then run into a vessel, with a perforated bottom, placed at the top of the shot tower. The arsenic, like any dissolved substance (compare p. 694), lowers the freezing-point of the solvent (lead), and delays the solidification of the lead until the drops have assumed perfect spherical form. At the foot of the tower the drops

fall into water and are cooled. The arsenic also renders the metal harder than pure lead, and less apt to be deformed during the explosion of the cartridge.

Compounds of arsenic are used (see Fig. 217) in glass works, in making arsenical sprays (mainly calcium arsenate), as weed-killers and insecticides, as cattle and sheep dip, and as hide preservatives.

The normal consumption in the United States amounts to about 30,000 metric tons (As_2O_3) per year. Of this amount about one-half is imported, mainly from Mexico.

Arsine AsH_3. — This substance corresponds in composition to ammonia and phosphine, and some of the ways in which it may be formed are analogous to those used in the case of these substances. Thus, when arsenic and zinc are melted together in the proportions to form **zinc arsenide** Zn_3As_2, and the product is treated with dilute hydrochloric acid, the result is similar to the action of water or dilute acids upon calcium phosphide. Arsine is evolved as a gas:

$$Zn_3As_2 + 6HCl \rightarrow 2AsH_3 + 3ZnCl_2.$$

Arsine (arsenuretted hydrogen) is also formed when a solution of arsenious chloride $AsCl_3$ or arsenic acid is added to zinc and hydrochloric acid in a generating flask:

$$AsCl_3 + 3H_2 \rightarrow AsH_3 + 3HCl.$$

This method, naturally, does not furnish pure arsine, for free hydrogen predominates in the gas. Pure arsine may be secured by leading the mixture with hydrogen through a **U**-tube immersed in liquid air. The arsine (b.-p. — 55°) condenses as a colorless liquid.

Arsine burns with a bluish flame, producing water and clouds of arsenic trioxide: $2AsH_3 + 3O_2 \rightarrow 3H_2O + As_2O_3$. The combustion of hydrogen containing arsine, generated as just described, produces the same substances. Since arsine, when heated, is readily dissociated into its constituents (compare p. 547), the vapor of free arsenic is present in the interior of such a hydrogen flame. This arsenic may be condensed in the form of a metallic-looking, brownish stain by interposition of a cold vessel of white porcelain (Fig. 122, p. 403). Even when only a trace of the compound of arsenic has been added to the materials in the generator, the stain which is produced is very conspicuous. This behavior thus furnishes us with an exceedingly delicate test — **Marsh's test** — for

the presence of arsenic in any soluble form of combination. The compounds of antimony alone show a similar phenomenon (see p. 864).

In carrying out the test, a tube of hard glass is attached to the generator, and is heated, by means of a Bunsen flame, at a point near to the flask. With this arrangement the arsenic is deposited in the form of a dark, lustrous ring just beyond the heated part. Zinc of special purity must be employed for generating the hydrogen, as all common specimens of the metal contain a sufficient amount of arsenic to give the metallic film without any actual addition of an arsenic compound, and a blank experiment must be run, with other portions of the same reagents, to guard against the possibility of its coming from any of them. Arsenic is more easily detected than any other poison which can be used in small amounts.

Arsine is exceedingly **poisonous,** the breathing of small amounts producing fatal effects. Organic derivatives of arsine have been used in warfare as "sneeze-producers" (see p. 656). It differs from ammonia more markedly than does phosphine, for it is not only without action on water and on acids, but does not unite directly even with the halides of hydrogen.

Halides of Arsenic.—The halides include a liquid **trifluoride** AsF_3, a gaseous **pentafluoride** AsF_5, a liquid **trichloride** $AsCl_3$ (arsenious chloride), a solid **tribromide** $AsBr_3$, and a solid **triiodide** AsI_3.

The **trichloride,** $AsCl_3$, which is easily prepared by passing chlorine gas into a vessel containing arsenic, is a colorless liquid, boiling at 130°. When mixed with water it is at once converted into the white, almost insoluble trioxide. The action is presumably similar to that of water upon the corresponding compound of phosphorus (p. 231), but the arsenious acid for the most part loses water and forms the insoluble anhydride:

$$AsCl_3 + 3H_2O \rightleftarrows As(OH)_3 + 3HCl,$$
$$2As(OH)_3 \rightleftarrows As_2O_3 \downarrow + 3H_2O.$$

This action, however, differs markedly from the other **in that it is reversible,** for arsenic trioxide interacts with aqueous hydrochloric acid, giving a solution of arsenious chloride (see p. 681). When this solution is boiled, the volatility of the arsenious chloride causes it to be carried over with the hydrochloric acid (b.-p. 110°, compare p. 556), and this method of separating arsenic from other substances is used in chemical analysis.

Oxides of Arsenic. — **Arsenic trioxide** As_2O_3 is produced by burning arsenic in the air and during the roasting of arsenical ores (p. 858), and is known as "white arsenic" or simply "arsenic." It is purified for commercial purposes by subliming the flue-dust in cylindrical pots. The pure trioxide is deposited in a glassy form in the upper part of the vessel. It passes slowly from this amorphous condition into the common crystalline variety. Its vapor density indicates that it possesses the molecular weight As_4O_6, but the simpler formula expresses its chemical properties sufficiently well.

When treated with water, the trioxide dissolves to a very slight extent (1.8 : 100 at 20°), forming arsenious acid, by reversal of the second of the equations shown on p. 860. As usual, the less stable, amorphous variety is the more soluble. In boiling water the solubility is much greater (11.5 : 100), but a condition of equilibrium is reached very slowly. With concentrated sulphuric acid the trioxide forms a salt of rather complex composition, indicating that it has feeble basic properties, but this "sulphate" is decomposed into the oxide and sulphuric acid when treated with water. When heated in a tube with carbon, this oxide is reduced (see p. 858), and the free element, being volatile, is deposited upon the cold part of the tube just above the flame. It is an active poison, since it gradually passes into solution in the system, forming arsenious acid. The fatal dose is 0.06–0.18 g. (1–3 grains), but "arsenic eaters" become tolerant of it and can take four times as much without evil effects.

The **pentoxide** As_2O_5 is a white crystalline substance, formed by heating arsenic acid: $2H_3AsO_4,H_2O \rightarrow As_2O_5 + 4H_2O$. When raised to a higher temperature, it loses a part of its oxygen, leaving the trioxide. In consequence of this instability, it cannot be formed by direct union of oxygen with the trioxide, as can phosphorus pentoxide.

Acids of Arsenic. — When elementary arsenic or arsenious oxide is treated with concentrated nitric acid, or with chlorine and water, **orthoarsenic acid** H_3AsO_4 is produced. The substance crystallizes as a deliquescent white solid $2H_3AsO_4,H_2O$. *Salts* of this acid, and of pyroarsenic acid $H_4As_2O_7$ and meta-arsenic acid $HAsO_3$, corresponding to the phosphoric acids (p. 550), are known. The two last acids, themselves, however, are not known as such. It has been shown by Menzies that, when the hemihydrate of orthoarsenic acid is dried at 100°, the only acid obtainable has the composition $H_5As_3O_{10}$ ($= 5H_2O,3As_2O_5$). When this acid is heated more strongly, it loses water, leaving the pentoxide As_2O_5. With

the phosphoric acids, the final elimination of all the water by simple heating is impossible (see p. 551). The chocolate-brown **silver orthoarsenate** Ag_3AsO_4 and the white $MgNH_4AsO_4$, like the corresponding phosphates, are insoluble in water.

Arsenious acid H_3AsO_3, like sulphurous and carbonic acids, loses water, and yields the anhydride, arsenic trioxide, when the attempt is made to obtain it from the aqueous solution. The **potassium** and **sodium arsenites,** K_3AsO_3 and Na_3AsO_3, are made by treating arsenic trioxide with caustic alkalies, and are much hydrolyzed by water. The arsenites of the heavy metals are insoluble, and can be made by precipitation. Paris green and Scheele's green (p. 792) are arsenites of copper. The poisonous effects of wall-paper colored with these compounds seem to be due to volatile organic derivatives of arsine which are formed by the action of a mould. In cases of poisoning by white arsenic, freshly precipitated ferric hydroxide (or the same compound in colloidal suspension) or magnesium hydroxide is administered, since by interaction with the arsenious acid they form insoluble arsenites. The salts of arsenious acid are readily oxidized, passing into arsenates. The action of a standard solution of iodine upon sodium arsenite, for example, is used in volumetric analysis:

$$Na_3AsO_3 + H_2O + I_2 \rightarrow Na_3AsO_4 + 2HI.$$

Sulphides of Arsenic. — Three sulphides of arsenic are known, As_2S_5, As_2S_3, As_2S_2. The first, **arsenic pentasulphide** As_2S_5, is obtained as a yellow powder by decomposition of the sulpharsenates (see p. 863), and by leading hydrogen sulphide into a solution of arsenic acid in *concentrated* hydrochloric acid. The latter action shows that the ion As^{+++++}, derived from $AsCl_5$, is present in the solution.

Arsenious sulphide As_2S_3 occurs in nature as orpiment, and was formerly used as a yellow pigment (*auripigmentum*). The word arsenic is derived from the Greek name for this mineral (ἀρσενικόν). It is obtained as a citron-yellow precipitate when hydrogen sulphide is led into an aqueous solution of arsenious chloride.

When hydrogen sulphide is led into an aqueous solution of arsenious acid, the sulphide is formed, but remains in **colloidal suspension.** It is a negatively charged colloid (p. 642). It is coagulated by adding solutions of salts, lower concentrations being sufficient the higher the valence of the positive ion of the salt (0.05 Molar KCl, 0.0007 *M* $BaCl_2$, 0.00009 *M* $AlCl_3$).

Realgar As_2S_2 is a natural sulphide of orange-red color, and is also manufactured by subliming a mixture of arsenical pyrite and pyrite:

$$2FeAsS + 2FeS_2 \rightarrow 4FeS + As_2S_2 \uparrow .$$

It burns in oxygen, forming arsenious oxide and sulphur dioxide, and is mixed with potassium nitrate and sulphur to make "Bengal lights."

Sulpharsenites and Sulpharsenates. — The sulphides of arsenic interact with solutions of alkali sulphides after the manner of the sulphides of tin (p. 827), giving soluble, complex sulphides. Arsenious sulphide with colorless ammonium sulphide gives ammonium sulpharsenite, and with the yellow sulphide gives ammonium sulpharsenate:

$$3(NH_4)_2S + As_2S_3 \rightarrow 2(NH_4)_3AsS_3,$$
$$3(NH_4)_2S + As_2S_3 + 2S \rightarrow 2(NH_4)_3AsS_4.$$

The formation of these soluble compounds is used in analysis (see p. 918). **Proustite** (p. 804) is a natural sulpharsenite of silver.

These salts are decomposed by acids, and give free sulpharsenious or sulpharsenic acid. These sulpho-acids, however, at once break up, giving hydrogen sulphide as a gas, and the sulphides of arsenic as yellow precipitates:

$$(NH_4)_3.AsS_3 + 3HCl \rightarrow 3NH_4Cl + H_3AsS_3 \rightarrow 3H_2S \uparrow + As_2S_3 \downarrow .$$
$$(NH_4)_3.AsS_4 + 3HCl \rightarrow 3NH_4Cl + H_3AsS_4 \rightarrow 3H_2S \uparrow + As_2S_5 \downarrow .$$

Antimony Sb

The Chemical Relations of the Element. — Antimony resembles arsenic in forming a hydride SbH_3 (also the unstable Sb_2H_2) and halides of the forms SbX_3 and SbX_5. The halides are partially hydrolyzed by water. The oxide Sb_2O_3 is basic as well as feebly acidic (amphoteric), and the oxide Sb_2O_5 is acidic. The compositions of the compounds are similar to those of the compounds of arsenic, but there are in addition salts, such as $Sb_2(SO_4)_3$, derived from the oxide Sb_2O_3. The element gives complex sulphides like those of arsenic.

Occurrence and Preparation. — Antimony occurs free in nature. The chief supply, however, is furnished by the black trisul-

phide Sb_2S_3, **stibnite,** which is found in Hungary, China and Japan, and forms shining, prismatic crystals of the rhombic system. Native stibnite is roasted in the air in order to remove the sulphur, and the white oxide which remains is mixed with carbon and reduced by strong heat:

$$Sb_2S_3 + 5O_2 \rightarrow Sb_2O_4 + 3SO_2,$$
$$Sb_2O_4 + 4C \rightarrow 2Sb + 4CO.$$

Alternatively, when stibnite is melted with iron, ferrous sulphide and free antimony are formed:

$$3Fe + Sb_2S_3 \rightarrow 2Sb + 3FeS.$$

The molten ferrous sulphide (sp. gr. 4.8) floats upon the molten antimony (sp. gr. 6.5), and the products, being mutually insoluble, are easily separated.

The annual consumption of antimony in the United States approximates 15,000 metric tons.

Properties. — Antimony is a white, crystalline metal (several unstable allotropic forms are also known), melting at 630° (b.-p. 1380°). It is brittle, and easily powdered. It is **used** in storage-battery plates and in making alloys such as Babbitt metal, type-metal, and britannia metal. The alloys of antimony expand during solidification, and therefore give exceptionally sharp castings.

The element unites directly with the halogens. It does not rust, but when heated it burns in the air, forming the trioxide Sb_2O_3 or a higher oxide Sb_2O_4. When heated with nitric acid, it yields the trioxide and, with more difficulty, antimonic acid H_3SbO_4. With hot concentrated sulphuric acid, it gives the sulphate $Sb_2(SO_4)_3$.

Stibine SbH_3. — The gaseous hydride of antimony SbH_3 is formed by the action of zinc and hydrochloric acid on any soluble compound of antimony. By the action of dilute, cold hydrochloric acid on an alloy of antimony and magnesium (1 : 2), a mixture of hydrogen and stibine containing as much as 11.5 per cent (by volume) of the latter may be made. It is separated by cooling with liquid air (b.-p. —17°). It is more easily dissociated than is arsine, and forms a deposit of antimony when a porcelain vessel is held in the flame. The behavior is in all respects similar to that of arsine (p. 859).

The layers of arsenic or antimony obtained upon white porcelain in Marsh's test (p. 859) may be distinguished readily in several ways. The arsenic spots are brownish in color, lustrous, and volatile. The antimony spots are black, smoky-looking, and involatile at the temperature of the Bunsen flame. The arsenic spots dissolve in a fresh solution of bleaching powder, producing calcium chloride and arsenic acid, while those of antimony are unaffected. The arsenic spots are scarcely attacked by a solution of yellow ammonium sulphide, while those of antimony dissolve readily, forming an ammonium sulphantimonate. Another distinction between arsine and stibine is found in their action upon a solution of nitrate of silver. Stibine precipitates a silver antimonide Ag_3Sb, and none of the antimony remains in the solution. Arsine, on the contrary, precipitates metallic silver, while arsenious acid remains in the solution.

Antimony Halides. — The halides include the **trichloride** $SbCl_3$, the **pentachloride** $SbCl_5$, the **tribromide** $SbBr_3$, **tri-iodide** SbI_3, **trifluoride** SbF_3, and **pentafluoride** SbF_5.

Antimony trichloride $SbCl_3$ is made by direct union of the elements. It forms large, soft crystals (m.-p. 73°, b.-p. 223°), and used to be named "butter of antimony." When treated with little water, it forms a white, opaque, insoluble basic salt, **antimony oxychloride**:

$$SbCl_3 + H_2O \rightleftarrows SbOCl\downarrow + 2HCl.$$

With a large amount of water, a greater proportion of the chlorine is removed, and $Sb_4O_5Cl_2$ ($= 2SbOCl,Sb_2O_3$) remains. With boiling water the oxide is finally formed. The action is not complete as long as hydrochloric acid is present. It may therefore be reversed, so that on addition of hydrochloric acid to the mixture a clear solution of the trichloride is re-formed. If the concentration of the acid is once more reduced by dilution with water, the oxychloride is again precipitated.

The **pentachloride** (m.-p. — 6°, b.-p. 140°) is formed by leading chlorine over the trichloride. It is a liquid which fumes strongly in the air, being hydrolyzed by the moisture.

Oxides of Antimony. — Three oxides are known: antimony trioxide Sb_2O_3, antimony pentoxide Sb_2O_5, and an intermediate oxide Sb_2O_4. The **trioxide** Sb_2O_3 (vapor density gives Sb_4O_6) is obtained by oxidizing antimony with nitric acid, or by combustion of antimony with a limited supply of oxygen. It is a white substance, insoluble in water. It is in the main a basic oxide, interacting with many acids to form salts of antimony, but it interacts also with alkalies, giving soluble **antimonites.** The **pentoxide**

Sb_2O_5 is a yellow, amorphous substance, obtained by heating antimonic acid. It combines only with bases to form salts, and is therefore an acid-forming oxide exclusively. The **tetroxide** Sb_2O_4 is formed by heating antimony or the trioxide in excess of oxygen. It is the most stable of the three oxides. It is neither acid- nor base-forming, and may be regarded (compare p. 832) as antimony antimonate ($SbSbO_4$).

The hydrated trioxide $Sb(OH)_3$ may be obtained as a white precipitate by adding dilute sulphuric acid to tartar-emetic (see below). It is insoluble, and easily loses water, giving the trioxide.

Salts of Antimony. — The **nitrate** $Sb(NO_3)_3$ and the **sulphate** $Sb_2(SO_4)_3$ are made by the interaction of the trioxide with nitric and sulphuric acids. They are hydrolyzed by water, giving basic salts, such as $(SbO)_2SO_4$, which, like $SbOCl$, are derived from the hydroxide $SbO(OH)$. When the trioxide is heated with a solution of potassium bitartrate $KHC_4H_4O_6$, a basic salt $K(SbO)C_4H_4O_6$, $\frac{1}{2}H_2O$, known as **tartar-emetic,** is formed. This is a white, crystalline substance which is soluble in water and is used in medicine. The univalent group SbO^{I} is known as **antimonyl,** and the above mentioned basic compounds are often called antimonyl sulphate, etc.

Antimonic Acid. — By vigorous oxidation of antimony with nitric acid, or by decomposing the pentachloride with water, a white, insoluble substance of the approximate composition H_3SbO_4 is obtained. This substance interacts with caustic potash and passes into solution. But the salts which have been made are pyro- and meta-antimonates. Thus, when antimony is fused with niter, **potassium meta-antimonate** $KSbO_3$ is formed. When dissolved, this salt takes up water, and forms a solution of the **acid potassium pyroantimonate:**

$$2KSbO_3 + H_2O \rightarrow K_2H_2Sb_2O_7.$$

If this is added to a concentrated solution of a salt of sodium, a **sodium pyroantimonate** $Na_2H_2Sb_2O_7$ is thrown down. This compound, almost the only somewhat insoluble salt of sodium (see p. 717), is formed also by direct action of sodium hydroxide upon antimonic acid.

Sulphides of Antimony. — There are two sulphides, the trisulphide Sb_2S_3 and the pentasulphide Sb_2S_5. The **trisulphide** Sb_2S_3

is found in nature as the black, crystalline stibnite. By the action of hydrogen sulphide upon solutions of salts of antimony, the trisulphide is precipitated as an orange-red powder, which, however, after having been melted, assumes the appearance of stibnite:

$$2SbCl_3 + 3H_2S \rightleftarrows Sb_2S_3 \downarrow + 6HCl.$$

The above action is reversed by concentrated hydrochloric acid, so that antimony trisulphide, like cadmium sulphide, can be precipitated only when the acid present is dilute (see p. 750).

The **pentasulphide** Sb_2S_5 is obtained by the decomposition of sulphantimonates (see below). In appearance it resembles the trisulphide and, when heated, it decomposes very readily into this substance and free sulphur. It is used for vulcanizing rubber.

Sulphantimonites and Sulphantimonates. — The behavior of the sulphides of antimony towards solutions of the alkali sulphides is very similar to that of the sulphides of arsenic (p. 863). The trisulphide dissolves in colorless ammonium sulphide with difficulty, forming an unstable soluble ammonium sulphantimonite:

$$Sb_2S_3 + 3(NH_4)_2S \rightarrow 2(NH_4)_3SbS_3.$$

With the pentasulphide, or with yellow ammonium sulphide, the action takes place more readily and soluble ammonium sulphantimonate is formed:

$$Sb_2S_5 + 3(NH_4)_2S \rightarrow 2(NH_4)_3.SbS_4,$$
$$Sb_2S_3 + 3(NH_4)_2S + 2S \rightarrow 2(NH_4)_3.SbS_4.$$

The most familiar substance of this class is **Schlippe's salt** Na_3-$SbS_4,9H_2O$. **Pyrargyrite** Ag_3SbS_3 (p. 804) is a mineral sulphantimonite.

When acids are added to solutions of sulphantimonates, the sulphantimonic acid which is liberated decomposes, and antimony pentasulphide is thrown down (see under Arsenic, p. 863).

Bismuth Bi

The Chemical Relations of the Element. — Bismuth forms an unstable compound BiH_3 with hydrogen. Its compounds with the halogens are of the form BiX_3 and are hydrolyzed by water giving basic salts. The oxide Bi_2O_3 is basic and the oxide Bi_2O_5, which

forms unstable bismuthates, is weakly acidic. Bismuth gives a carbonate, nitrate, sulphate, phosphate, and other salts, in all of which it acts as a trivalent element. It forms no soluble complex sulphides.

Occurrence and Properties. — This element is found free in nature, and also to some extent as trioxide Bi_2O_3 and trisulphide Bi_2S_3. It is a shining, brittle metal with a reddish tinge (m.-p. 271°). Bismuth, like antimony, is one of the few substances (see p. 163) which expand on solidifying.

Mixtures of bismuth with other metals of low melting-point fuse at lower temperatures than do the separate metals. This is another illustration of the fact that a solution melts at a lower temperature than the pure solvent (p. 216). Thus, **Wood's metal,** containing bismuth (m.-p. 271°) 4 parts, lead (m.-p. 327°) 2 parts, tin (m.-p. 232°) 1 part, and cadmium (m.-p. 321°) 1 part, melts at 60.5°, considerably below the boiling-point of water. Alloys of this class are used as plugs in sprinkler systems and as stops to hold steel fire-doors open. When, in consequence of a fire, the temperature rises, the alloy melts, the water exits are opened and the fire-doors swing shut. Safety plugs in steam boilers, made of a similar, but less fusible alloy, melt when, as the result of failure of the safety valve, the steam pressure, and therefore the temperature, exceeds a predetermined value. They behave in the same way when the water is dangerously low and the metal above the water becomes too hot.

Bismuth does not tarnish, but when treated strongly it burns to form the trioxide. With the halogen it forms a **fluoride** BiF_3, a **bromide** $BiBr_3$, and an **iodide** BiI_3. When the metal is treated with oxygen acids, or the trioxide with any acids, salts are produced.

Compounds of Bismuth. — In addition to the basic **trioxide** Bi_2O_3, which is the yellow powder obtained by direct oxidation of the metal or by ignition of the nitrate, and the weakly acidic **pentoxide** Bi_2O_5, two other oxides are known — BiO and Bi_2O_4. Neither of these, however, is either acid-forming or base-forming.

The salts of trivalent bismuth, when dissolved in water, like those of antimony, give insoluble basic salts, and the actions are reversible, the basic salts being redissolved by addition of an excess of the acid. In the case of the **chloride** $BiCl_3,H_2O$ and the **nitrate** $Bi(NO_3)_3,5H_2O$, the actions taking place are:

$$BiCl_3 + 2H_2O \rightleftarrows Bi(OH)_2Cl + 2HCl,$$
$$Bi(NO_3)_3 + 2H_2O \rightleftarrows Bi(OH)_2NO_3 + 2HNO_3.$$

The former of these products, when dried, loses a molecule of water, giving the **oxychloride** $BiOCl$. The **oxynitrate** of bismuth $Bi(OH)_2NO_3$ is much used in medicine, for the treatment of some forms of indigestion, under the name "subnitrate of bismuth." It is often contained in face powders.

The brownish-black, insoluble **trisulphide** Bi_2S_3 may be obtained by direct union of the elements, or by precipitation with hydrogen sulphide. On addition of much acid the second of the above actions is reversed. This sulphide is not affected by solutions of ammonium sulphide or of potassium sulphide. It differs, therefore, markedly from the sulphides of arsenic and antimony in its behavior.

The Family as a Whole

When we compare the elements of this group, taking nitrogen as the first of the family, in spite of the fact that it is somewhat less closely related to the other members than they are to one another, we find an admirable illustration of the general principles which the periodic system presents.

The elements themselves change progressively in physical properties as the atomic weight increases. Nitrogen is a gas which with sufficient cooling yields a white solid, phosphorus is a white, or a red solid, and arsenic, antimony, and bismuth are metallic in appearance. The first combines directly with hydrogen, the remainder give hydrides, of increasing instability, indirectly. The hydride of nitrogen combines with water to form a base, while the other hydrides show no such tendency. Ammonia unites with all acids, including those of the halogens, to form salts; phosphine with the hydrogen halides only; the others do not combine with acids at all. As regards their metallic properties, in the chemical sense, nitrogen and phosphorus do not by themselves form positive ions, and furnish us therefore with no salts whatever. Arsenic gives a trivalent positive ion, which is found in solutions of the halides only. It forms no normal sulphates, nitrates, or other salts. Antimony and bismuth both give trivalent positive ions. The sulphates, nitrates, etc., of antimony, however, are readily decomposed by water with precipitation of the hydroxide. The salts of bismuth, on the other hand, do not readily give the pure hydroxide with water, although they are easily hydrolyzed to basic salts.

The halogen compounds of nitrogen and phosphorus are completely hydrolyzed by water, and do not exist when any water is

present, even when excess of the halogen acid is used. The halogen compounds of arsenic are also hydrolyzed by cold water, but exist in solution in presence of excess of the acids. The halogen compounds of antimony and bismuth are incompletely hydrolyzed by cold water.

Each element gives a trioxide and a pentoxide. With nitrogen these are acid-forming, being the anhydrides of nitrous and nitric acids. With phosphorus the trioxide and the pentoxide are anhydrides of acids. With arsenic the trioxide is basic towards the halogen acids, and is the first example of a basic oxide which we encounter in this group. The pentoxide, however, is acid-forming. The trioxide of antimony is mainly base-forming, although it is feebly acid-forming also. The pentoxide is acid-forming. The trioxide of bismuth is base-forming exclusively, and the pentoxide only very weakly acid-forming.

These statements, which could easily be expanded, are sufficient to show that when the periodic law is borne in mind it furnishes valuable aid in systematizing the chemistry of a group like this.

Analytical Reactions of Arsenic, Antimony. and Bismuth. — The ions which are most frequently encountered are As^{+++}, Sb^{+++}, Bi^{+++}, $AsO_4^{\equiv}$, and $AsO_3^{\equiv}$. The first three, with hydrogen sulphide, give colored sulphides which are not affected by dilute acids. The sulphides of arsenic and antimony are separable from the sulphide of bismuth by solution in yellow ammonium sulphide. The ion of the arsenates $AsO_4^{\equiv}$ is identified by its interaction with salts of silver and the formation of $MgNH_4AsO_4$, while that of the arsenites $AsO_3^{\equiv}$ is recognized by its reducing power. Marsh's test (p. 859) enables us to recognize the presence of traces of compounds of arsenic and antimony. Oxygen compounds of arsenic, when heated with carbon, give a volatile, metallic-looking deposit of arsenic.

Vanadium, Columbium, Tantalum, Protoactinium

These four elements occupy the left-hand side of the sixth column in the periodic system (p. 446). All are rare, but **vanadium** is less uncommon than the others. It is found in rather complex compounds. When these are heated with soda and sodium nitrate, **sodium metavanadate** $NaVO_3$ is formed, and can be extracted with water. Solid ammonium chloride is added to the solution, and ammonium metavanadate NH_4VO_3, which is less soluble in solu-

tions of salts of ammonium (compare p. 757) than in water, appears in the form of yellow crystals. When this salt is heated, **vanadic anhydride** V_2O_5, a yellowish-red powder, remains. This oxide interacts with bases giving vanadates, of which the most stable are the metavanadates. The element forms several **chlorides,** such as VCl_2, VCl_3, VCl_4, $VOCl_3$, and five **oxides,** V_2O, VO, V_2O_3, VO_2, and V_2O_5. The element has very feeble base-forming properties, and gives only a few, unstable salts. Ferrovanadium, an alloy with iron, is used in making vanadium steel (see p. 902). Vanadium pentoxide V_2O_5 has recently come into extensive use as a catalyst in the contact sulphuric acid process (p. 420). It is claimed to be as efficient as platinum, and much more resistant to poisons.

Columbium (or niobium), first discovered and named by Hatchett (1801), and **tantalum** likewise possess feebly base-forming properties, their chief compounds being the columbates and tantalates. Tantalum-steel alloys are used in the construction of acid-resisting apparatus.

Protoactinium is the parent element of the actinium series of radioactive disintegrations (see p. 468), its half-life being 20,000 years. Small quantities have recently been extracted from radium wastes.

Exercises. — 1. How do you account for the fact that the molecular weight of arsenic at 644° (p. 858) is not exactly 300, and why is 308.4 ÷ 4 not accepted as the atomic weight?

2. What should you expect to be the interaction of arsine with concentrated nitric acid?

3. Formulate in detail the changes involved in the solution of arsenic trioxide and the interaction of hydrochloric acid with the arsenious acid so formed.

4. What is the full significance of the fact that arsenic pentasulphide may be precipitated by hydrogen sulphide from a solution of arsenic acid in hydrochloric acid? Make the equation.

5. To what classes of chemical changes do the interactions of arsenious sulphide and antimony trisulphide with yellow ammonium sulphide belong?

6. Construct equations showing the interaction of, (*a*) concentrated sulphuric acid and antimony, (*b*) arsenic and chlorine-water, (*c*) antimony and yellow ammonium sulphide, (*d*) silver nitrate and stibine, (*e*) potassium hydroxide and arsenic trioxide, (*f*) concentrated nitric acid and antimony, (*g*) acids and ammonium orthosulphantimonate.

7. How should you set about making Schlippe's salt?

8. What volume will 74.96 g. of arsenic vapor, under 1 atmosphere pressure, occupy, (*a*) at 644°, (*b*) at 1700°? Assume the formulæ As_4 and As_2 respectively.

9. What weight of arsenic will be required to make 1000 kg. of calcium arsenate?

10. What is the percentage of arsenic in Paris green (p. 792), the formula for which is $Cu_3(AsO_3)_2,Cu(C_2H_3O_2)_2$? What is the chemical name for this substance? What kind of a salt is it? What is its percentage of copper?

11. Balance the following equations by the ion and electron method:

$$(a)\ As + HNO_3 \rightarrow H_3AsO_4 + NO + H_2O$$
$$(b)\ Na_3AsO_3 + H_2O + I_2 \rightarrow Na_3AsO_4 + HI.$$

READING REFERENCES

Weeks; The Discovery of Arsenic, Antimony and Bismuth. Journal of Chemical Education, 9, 11, 1932.

Weeks; The Discovery of Columbium, Tantalum and Vanadium. Journal of Chemical Education, 9, 863, 1932.

CHAPTER LI

CHROMIUM AND MANGANESE

The **chromium** (Cr, atomic number 24) family includes **molybdenum** (Mo, at. no. 42), **tungsten** (W, at. no. 74), and **uranium** (U, at. no. 92), and occupies the left side of the seventh column of the periodic table, with the sulphur family on the right side.

The features which are common to the four elements are also those which affiliate them most closely with their neighbors on the right side of the column. They yield oxides of the forms CrO_3, MoO_3, WO_3, and UO_3, which, like SO_3, are acid anhydrides, and show the elements to be sexivalent. They give also acids of the form H_2XO_4, such as chromic acid H_2CrO_4. These acids correspond to sulphuric acid, and their salts, for example the chromates, resemble the sulphates. Thus, sodium chromate $Na_2CrO_4,10H_2O$ is isomorphous with Glauber's salt (p. 207), and potassium chromate K_2CrO_4 with potassium sulphate.

Aside from the chromates, the first element forms also two basic hydroxides $Cr(OH)_2$ and $Cr(OH)_3$, from which the numerous chromous (Cr^{++}) and chromic (Cr^{+++}) salts are derived. Uranium forms a dioxide UO_2, to which correspond the uranous salts like $U(SO_4)_2$, but the most familiar salts of this metal are basic salts of the oxide UO_3, and have the form $UO_2(NO_3)_2$. Molybdenum and tungsten are not base-forming elements.

CHROMIUM Cr

The Chemical Relations of the Element. — Chromium gives four classes of compounds, and most of them are colored substances (Greek *χρωμα*, color). The **chromates** are derived from chromic acid H_2CrO_4, which, however, is itself unstable, and leaves the anhydride CrO_3 when its solution is evaporated. The oxide and hydroxide in which the element is trivalent, namely Cr_2O_3 and $Cr(OH)_3$, are weakly basic and still more weakly acidic. Hence we have **chromic salts** such as $CrCl_3$ and $Cr_2(SO_4)_3$ which are somewhat hydrolyzed, but no carbonate, and no sulphide which is stable in water. The compounds in which the same hydroxide acts as an acid are the **chromites,** and are derived from the less completely hydrated form of the oxide $CrO(OH)$. Potassium chromite $KCrO_2$

is more easily hydrolyzed, however, than is potassium zincate or potassium aluminate. Finally, the **chromous salts,** such as $CrCl_2$ and $CrSO_4$, correspond to chromous hydroxide $Cr(OH)_2$, in which the element is bivalent. This hydroxide is more distinctly basic than is chromic hydroxide, and forms a carbonate and sulphide which can be precipitated in aqueous solution. The chromous salts resemble the stannous and ferrous salts (see p. 904) in being easily oxidized by the air.

Occurrence and Isolation. — Chromium is found chiefly in ferrous chromite $Fe(CrO_2)_2$, which constitutes the mineral **chromite.** This is mined chiefly in California, Rhodesia, and New Caledonia. The U. S. production in 1918, stimulated by war requirements, exceeded 80,000 tons. In 1934 is sank to less than 350 tons. The element also occurs in nature in **crocoisite** $PbCrO_4$, which is chromate of lead. It was first discovered in the latter mineral by Vauquelin (1797). The metal is easily made by reduction of the oxide with aluminium filings by Goldschmidt's method (p. 770).

Physical and Chemical Properties. — Chromium is a white, crystalline, very hard metal (m.-p. 1615°). It does not tarnish, but when heated it burns in oxygen, giving the green chromic oxide Cr_2O_3. It seems to exist in two states, an active and a passive one, the relations of which are still somewhat obscure. A fragment which has been made by the Goldschmidt method, or has been dipped in nitric acid, is passive, and does not displace hydrogen from hydrochloric acid. When, however, the specimen is warmed with this acid, it begins to interact, and thereafter behaves as if it lay between zinc and cadmium in the electromotive series. If left in the air, it slowly becomes inactive again.

Tin and iron with hydrochloric acid form stannous and ferrous chlorides respectively, because the higher chlorides, if present, would be reduced by the displaced hydrogen. Here, for the same reason, chromous chloride and not chromic chloride is formed:

$$Cr + 2H^+ \rightarrow Cr^{++} + H_2.$$

Chromium (3 per cent) is added to harden steel, and with nickel is used in armor-piercing shells and in **armor plate.** Alloys which, although composed entirely of active metals, are hardly affected even by boiling acids (including nitric acid), usually contain chromium (*e.g.*, 60 per cent Cr, 36 per cent Fe, 4 per cent Mo, no C).

Stainless cutlery contains 12 to 14 per cent of chromium. Chromium electroplating (on motor cars, etc.) is extremely resistant to corrosion, and is coming into extensive use.

Derivatives of Chromic Acid

Potassium Chromate K_2CrO_4. — This and the sodium salt, or rather the corresponding dichromates (see below), are made directly from chromite, and form the starting-point in the preparation of the other compounds of chromium. Finely powdered chromite is mixed with potash and limestone, and roasted. The lime is employed chiefly to keep the mass porous and accessible to the oxygen of the air, the potassium compounds being easily fusible:

$$4Fe(CrO_2)_2 + 8K_2CO_3 + 7O_2 \rightarrow 2Fe_2O_3 + 8K_2CrO_4 + 8CO_2.$$

The iron is oxidized to ferric oxide, and the chromium passes from the state of chromic oxide in the chromite (FeO,Cr_2O_3) to that of chromic anhydride in the potassium chromate (K_2O,CrO_3). The cinder is treated with hot potassium sulphate solution. This interacts with the calcium chromate, which is formed at the same time, giving insoluble calcium sulphate:

$$CaCrO_4 + K_2SO_4 \leftrightarrows CaSO_4 \downarrow + K_2CrO_4.$$

The whole of the potassium chromate goes into solution.

Potassium chromate is pale-yellow in color, gives anhydrous, rhombic crystals like those of potassium sulphate, and is very soluble in water (61 : 100 at 10°).

Sodium chromate $Na_2CrO_4,10H_2O$ is made by using sodium carbonate in the process just described.

The Dichromates. — When a solution of potassium sulphate is mixed with an equivalent amount of sulphuric acid, potassium bisulphate is obtainable by evaporation: $K_2SO_4 + H_2SO_4 \rightarrow 2KHSO_4$. The *dry* acid salt, when *heated*, loses water (p. 429), giving the pyrosulphate (disulphate): $2KHSO_4 \rightleftarrows K_2S_2O_7 + H_2O$, but the latter, when redissolved, returns to the condition of acid sulphate. The second action, therefore, is instantly reversed in presence of water. Now, when an acid is added to a chromate we should expect the chromic acid H_2CrO_4, thus liberated, to interact similarly giving an acid chromate (say, $KHCrO_4$). No acid chromates are known, however, and instead of them, pyrochromates or dichro-

mates are produced, with elimination of water. Thus, with sulphuric acid, we obtain the reaction:

$$2K_2CrO_4 + H_2SO_4 \rightarrow K_2Cr_2O_7 + H_2O + K_2SO_4.$$

Potassium dichromate is made commercially by adding sulphuric acid to the crude solution of the chromate obtained from chromite (p. 875). It crystallizes when the liquid cools, and the mother-liquor, containing the potassium sulphate and undeposited dichromate, is used for extracting a fresh portion of cinder. As the dichromates are much less soluble than the chromates, they crystallize from less concentrated solutions, and can therefore be obtained in purer condition.

Potassium dichromate $K_2Cr_2O_7$ crystallizes in asymmetric tables of orange-red color. Its solubility in water is 8 : 100 at 10° and 12.5 : 100 at 20°. **Sodium dichromate** $Na_2Cr_2O_7,2H_2O$ forms red crystals also, and its solubility is 109 : 100 at 15°. This salt is now cheaper than potassium dichromate, and has largely displaced the latter for commercial purposes (compare p. 704).

By treatment of the chromates with larger amounts of free acid, other polychromates are formed. Thus, with increasing amounts of nitric acid, ammonium chromate gives first the dichromate $(NH_4)_2Cr_2O_7$, which may be written $(NH_4)_2CrO_4,CrO_3$, then the trichromate $(NH_4)_2CrO_4,2CrO_3$, and even the **tetra**chromate $(NH_4)_2CrO_4,3CrO_3$, all of which are red crystalline substances.

Chemical Properties of the Dichromates. — 1. When concentrated sulphuric acid is added to a dichromate (or chromate), **chromic anhydride** CrO_3 separates in red needles.

$$Na_2Cr_2O_7 + H_2SO_4 \rightarrow Na_2SO_4 + H_2O + 2CrO_3\downarrow.$$

2. Although a dichromate lacks the hydrogen, it is essentially of the nature of an acid salt, just as SbOCl lacks hydroxyl, but is essentially a basic salt. Hence, when potassium hydroxide is added to a solution of potassium dichromate, potassium chromate is formed:

$$K_2Cr_2O_7 + 2KOH \rightarrow 2K_2CrO_4 + H_2O.$$

The solution changes from red to yellow, and the chromate is obtained by evaporation. In this way the pure alkali chromates are most readily made.

3. By addition of potassium dichromate to a solution of a salt

of a metal whose chromate is insoluble, the chromate and *not* the dichromate is precipitated:

$$2Ba(NO_3)_2 + K_2Cr_2O_7 + H_2O \rightleftarrows 2BaCrO_4 \downarrow + 2KNO_3 + 2HNO_3.$$

4. The dichromates of potassium and sodium melt when heated and, at a white heat, decompose, giving the chromate, chromic oxide, and free oxygen:

$$4K_2Cr_2O_7 \rightarrow 4K_2CrO_4 + 2Cr_2O_3 + 3O_2.$$

5. With free acids the dichromates give powerful oxidizing mixtures, in consequence of their tendency to form chromic salts. When concentrated hydrochloric acid is used, this acid itself (see p. 240) suffers oxidation:

$$K_2Cr_2O_7 + 14HCl \rightarrow 2KCl + 2CrCl_3 + 7H_2O + 3Cl_2.$$

When sulphuric acid is employed, an oxidizable substance such as hydrogen sulphide (compare p. 405), sulphurous acid, or alcohol must be present, if the dichromate is to be reduced. In practice, this sort of action is used for the purpose of making chromic salts, and for its oxidizing effects, as in the preparation of acetaldehyde (p. 582) from alcohol and in the dichromate battery.

6. When a body which is not merely oxidizable, but is an active reducing agent, is employed, the dichromate may be reduced without the addition of any acid. For example, when warmed with ammonium sulphide, a dichromate gives chromic hydroxide and free sulphur:

$$K_2Cr_2O_7 + 3(NH_4)_2S + 7H_2O \rightarrow 2Cr(OH)_3 + 3S + 2KOH + 6NH_4OH.$$

Applications of Dichromates. — If the reducing agent is less active, the change may nevertheless take place under the influence of light. Thus, when paper is coated with gelatine containing a soluble chromate or dichromate, and, after being dried, is exposed to light, chromic oxide is formed by reduction, and combines with the gelatine. This product will not swell up or dissolve in tepid water, as does pure gelatine. This action is used in many ways for purposes of artistic reproduction. Thus, if the gelatine mixture is made up with lampblack and, after the coating has dried, is covered with a negative and exposed to light, the parts which were protected from illumination may afterwards be washed away, while the

carbon print remains. The gelatine layer can be transferred to wood or copper before washing. When materials of different colors are substituted for the lampblack, prints of any desired tint may be made by the same process.

Sodium dichromate is used, instead of tan-bark, in **tanning** kid and glove leathers (**chrome-tanning process**). A reducing agent is employed to precipitate chromic hydroxide $Cr(OH)_3$ in the leather. Its use diminishes the time required for the process from 8 or 10 months to a few hours. The hide is a mixture of colloidal materials, and the hydroxide is adsorbed.

Insoluble Chromates. — A number of chromates, formed by precipitation with a solution of a soluble chromate or dichromate, are familiar. Thus, **lead chromate** $PbCrO_4$ is used as a yellow pigment. By treatment with lime-water it gives a basic salt of brilliant orange color — **chrome-red** Pb_2OCrO_4. Salts of calcium give a yellow, hydrated **calcium chromate** $CaCrO_4,2H_2O$ analogous to gypsum, and, like it, perceptibly soluble in water (0.4 : 100 at 14°). **Barium chromate** $BaCrO_4$ is also yellow. It interacts with active acids to form the dichromate, and passes into solution. It is not soluble enough to be attacked by acetic acid. **Strontium chromate** $SrCrO_4$, however, is soluble in acetic acid. **Silver chromate** Ag_2CrO_4 is red, and interacts easily with acids. It will be observed that there is a close correspondence between the relative solubilities (see Table) of the chromates and the sulphates.

Chromyl Chloride CrO_2Cl_2. — This compound corresponds to sulphuryl chloride SO_2Cl_2, and is made by distilling a dichromate with a chloride and concentrated sulphuric acid:

$$K_2Cr_2O_7 + 4KCl + 3H_2SO_4 \rightarrow 2CrO_2Cl_2 + 3K_2SO_4 + 3H_2O.$$

The hydrochloric acid liberated from the chloride may be supposed to interact with chromic acid from the dichromate:

$$CrO_2(OH)_2 + 2HCl \rightleftarrows CrO_2Cl_2 + 2H_2O.$$

Chromyl chloride is a red liquid (b.-p. 118°). It fumes strongly in moist air, being hydrolyzed by water (read the last equation backwards). The corresponding bromine and iodine compounds are unstable, and when a bromide or iodide is treated as described above, the halogens are liberated by oxidation, and no volatile compound of chromium appears. Hence, when an unknown halide is

mixed with potassium dichromate and sulphuric acid and distilled, and the vapors are caught in ammonium hydroxide, the finding of a chromate in the distillate demonstrates the existence of a chloride in the original mixture:

$$CrO_2Cl_2 + 4NH_4OH \rightarrow (NH_4)_2CrO_4 + 2NH_4Cl + 2H_2O.$$

This action is used as a test for the presence of traces of chlorides in large amounts of bromides or iodides, or both.

Chromic Anhydride CrO_3. — This oxide is made as described above (par. 1, p. 876), and is often called "chromic acid." It is soluble in water, and combines with the latter to some extent, giving dichromic acid $H_2Cr_2O_7$. In a solution acidified with an active acid it is much used as an oxidizing agent for organic substances. It interacts with acids in the same way as do the dichromates, giving chromic salts and furnishing oxygen to the oxidizable body. When heated by itself, it loses oxygen readily, leaving the green chromic oxide: $4CrO_3 \rightarrow 2Cr_2O_3 + 3O_2$.

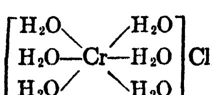
Chromic and Chromous Compounds

Chromic Chloride. — A **hydrated chloride** $CrCl_3,6H_2O$ is obtained by reducing potassium dichromate with hydrochloric acid (p. 877) and allowing the partially evaporated solution to crystallize. When heated, it is hydrolyzed, and chromic oxide remains. The **anhydrous chloride** $CrCl_3$ is formed by sublimation, as a mass of brilliant, reddish-violet scales, when chlorine is led over heated metallic chromium.

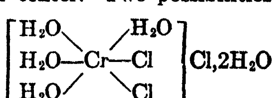
The anhydrous salt dissolves with extreme slowness, even in boiling water, but in presence of a trace of chromous chloride or stannous chloride it is easily soluble. The solution is green, as are all solutions of chromic salts after they have been boiled, but on standing in the cold, bluish crystals of $CrCl_3,6H_2O$ are deposited. These give a violet solution with cold water, but boiling reproduces the green color. The difference in the two solutions is due to the different ions furnished by hydrated chromic chloride under different conditions. From the green solution, which contains $[Cr(H_2O)_4Cl_2]^+$ and Cl^-, silver nitrate precipitates immediately only one-third of the chlorine as silver chloride. From the violet solution, which contains $[Cr(H_2O)_6]^{+++}$ and $3Cl^-$, all of the chlorine is at once precipitated.

In the explanation of the differences of behavior between the violet and the green solutions of chromium chloride, as well as in the systematic study of the numerous complex compounds of chromium, platinum, cobalt, etc., the Werner theory of **auxiliary valence** (p. 526) has proved of invaluable service. It will be recalled that, according to the theory of Werner, there can be assigned to each element a **co-ordination number**, which represents the maximum number of atoms, radicals or molecular groups that can be directly combined with an atom of the element, functioning as the center of a complex nucleus. The co-ordination number of nitrogen being four, the radical NH_4 affords a simple example of such a nucleus. In this nucleus the specific characteristics not only of the hydrogen, but also of the nitrogen, are completely lost; the nucleus functions as a distinct "compound radical." The co-ordination number being completed, any residual atoms or groups in the molecule of derivatives of this radical must be located outside the nucleus. Such atoms or groups are combined with no specific part of the nucleus, but distribute their affinity over the compound radical as a whole. In ammonium chloride, for instance, the chlorine atom is assumed, under the Werner theory, to be combined with the NH_4 group *as a whole*, not with the nitrogen atom or any particular hydrogen atom. As a result of their position and of this indefinite linkage, the outside atoms or groups are very readily split off, *e.g.*, as ions in aqueous solutions. Thus we have, with ammonium chloride, the ions $[NH_4]^+$ and Cl^-. The charge on the nucleus must obviously be equal and opposite in sign to the total charge assumed by the exterior atoms or groups, when they split off as ions.

In the case of chromium, the *co-ordination number* is **six**, and the hexahydrate of chromium chloride $CrCl_3,6H_2O$ may be given several different formulæ, according to the way in which we arrange the rest of the molecule around the chromium atom as a nuclear center. Two possibilities are written below:



I.



II.

Examining the first formula in the light of what has been said above, we conclude that all three chlorine atoms will be ionizable, and that in aqueous solution the substance will dissociate into $[Cr(H_2O)_6]^{+++}$ and $3Cl^-$. A substance represented by the second formula, however, contains only one exterior chlorine atom, and in aqueous solution its dissociation will be restricted to $[Cr(H_2O)_4Cl_2]^+$ and Cl^-. Formula I typifies, in short, the behavior of the violet variety of the salt, and formula II the behavior of the green variety. A solution of the former gives up all of its chlorine on precipitation with silver nitrate, a solution of the latter only one-third. It may be noted that a third isomer is known, also green in color, with the intermediate formula $[Cr(H_2O)_5Cl]Cl_2,H_2O$.

The co-ordination number is independent of the nature of the radicals or groups directly linked with the central atom, so that we may replace either the water groups or the chloride radicals in the nuclei of the above compounds by other groups, such as NH_3, and by other negative radicals, such as bromide Br or nitrite NO_2. It would carry us too far here to go into the detailed consequences in each particular case, and we shall accordingly defer the matter until we reach the complex compounds of cobalt, when a typical series of replacements will be briefly discussed (see p. 912).

Chromic Hydroxide. — When ammonium hydroxide is added to a solution of a chromic salt, a hydrated hydroxide of pale-blue color, $2Cr(OH)_3,H_2O$, is thrown down. This loses water by stages, giving intermediate hydroxides such as $Cr(OH)_3$ and $CrO(OH)$, and finally Cr_2O_3. It interacts with acids, giving chromic salts. It also dissolves in potassium and sodium hydroxides to form green solutions of **chromites** of the form $KCrO_2$. When the solutions of the alkali chromites are boiled, the free chromic hydroxide, present in consequence of hydrolysis, is converted into a greenish, less completely hydrated, and less soluble variety. This begins to come out as a precipitate, and soon the whole action is reversed. Insoluble chromites, such as that of iron $Fe(CrO_2)_2$, are found in nature. Many of them, like $Zn(CrO_2)_2$ and $Mg(CrO_2)_2$, may be formed by fusing the oxide of the metal with chromic oxide; the action being similar to that used in making zincates (p. 748) and aluminates (p. 771). The hydroxide is used as a mordant (p. 648) and is the active substance in the chrome-tanning process (p. 878).

Chromic Oxide Cr_2O_3. — This oxide is obtained as a green, infusible powder by heating the hydroxide, or, more readily, by heating dry ammonium dichromate; or by igniting potassium dichromate with sulphur and washing the potassium sulphate out of the residue:

$$(NH_4)_2Cr_2O_7 \rightarrow N_2 + 4H_2O + Cr_2O_3,$$
$$K_2Cr_2O_7 + S \rightarrow K_2SO_4 + Cr_2O_3.$$

Chromic oxide is not affected by acids, but may be converted into the sulphate by fusion with potassium bisulphate. It is **used** for making green paint, and for giving a green tint to glass. When the oxide, or any of the chromic salts, is fused with a basic substance such as an alkali carbonate, it passes into the form of a chromate, absorbing the necessary oxygen from the air. If an alkali nitrate or chlorate is added, the oxidation goes on more quickly. The alkaline solution of the chromites may be oxidized, for example, by addition of chlorine or bromine, and chromates are formed.

Chromic Sulphate. — This salt crystallizes in reddish-violet crystals $Cr_2(SO_4)_3,15H_2O$, and may be made by treating the hydroxide with sulphuric acid. When mixed with potassium sulphate, it gives beautiful reddish-violet, octahedral crystals of **chrome-alum**

$K_2SO_4,Cr_2(SO_4)_3,24H_2O$ (see p. 775). This double salt is most easily obtained by reducing potassium dichromate in dilute sulphuric acid by means of sulphurous acid (p. 877), and allowing the solution to crystallize. The solution of the crystals, either of the pure sulphate or of the alum, is bluish-violet (hydrated Cr^{+++}), but when boiled becomes green (compare chromic chloride).

Chromous Compounds. — By the interaction of chromium with hydrochloric acid, or by reducing chromic chloride in a stream of hydrogen, **chromous chloride** $CrCl_2$ is formed. The anhydrous salt is colorless, and its solution is light blue (Cr^{++}). Like stannous chloride, it is very easily oxidized by the air, a solution of it containing excess of hydrochloric acid being used in the laboratory to absorb oxygen:

$$4CrCl_2 + 4HCl + O_2 \rightarrow 4CrCl_3 + 2H_2O.$$

Chromous hydroxide $Cr(OH)_2$ is obtained as a yellow precipitate when alkalies are added to the chloride. With sulphuric acid it gives **chromous sulphate** $CrSO_4,7H_2O$, which is one of the vitriols (p. 749).

Chromous salts give with ammonium sulphide a black precipitate of **chromous sulphide** CrS, and with sodium acetate a red precipitate of **chromous acetate.** The latter is not very soluble, and is less quickly oxidized by the air than any of the other chromous compounds.

Analytical Reactions of Chromium Compounds. — The chromic salts give either the bluish-violet chromic-ion Cr^{+++}, or the green complex cations, and may be recognized in solution by their color. The chromates and dichromates give the ions $CrO_4^{=}$ and $Cr_2O_7^{=}$, which are yellow and red respectively. From chromic salts, alkalies and ammonium sulphide precipitate the bluish-green hydroxide, and carbonates give a basic carbonate which is almost completely hydrolyzed to hydroxide. By fusion with sodium carbonate and sodium nitrate, they yield a yellow bead containing the chromate. The chromates and dichromates are recognized by the insoluble chromates which they precipitate, and by their oxidizing power when mixed with acids. All compounds of chromium give a green borax bead containing chromic borate, and this bead differs from that given by compounds of copper (see p. 793), both in tint and in being unreducible.

Molybdenum, Tungsten, Uranium

Molybdenum. — This element is found chiefly in **wulfenite** $PbMoO_4$ and **molybdenite** MoS_2. The latter resembles black lead (graphite), and its appearance suggested the name of the element (Greek μολύβδαινα, lead). The molybdenite is converted by roasting into **molybdic anhydride** MoO_3. When this is treated with ammonium hydroxide, or with sodium hydroxide, **ammonium molybdate** $(NH_4)_2MoO_4$ or **sodium molybdate** $Na_2MoO_4,10H_2O$ is obtained. The **metal** itself is liberated by reducing the oxide or chloride with hydrogen. When pure it is a silvery metal and, like iron (p. 901), takes up carbon and shows the phenomena of tempering. It is used in making molybdenum-steel alloys. The **oxides** Mo_2O_3, MoO_2, and MoO_3 are known, but the lower oxides are not basic. The **chlorides** Mo_3Cl_6, $MoCl_3$, $MoCl_4$, and $MoCl_5$ have been made.

The chief use of molybdenum compounds in the laboratory is in **testing for** and estimating **phosphoric acid.** When a little of a phosphate is added to a solution of ammonium molybdate in nitric acid, and the mixture is warmed, a copious yellow precipitate of a complex **phosphomolybdate of ammonium** is formed. This compound is soluble in excess of phosphoric acid and in alkalies, but not in dilute mineral acids.

Tungsten. — The minerals **scheelite** $CaWO_4$ and **wolfram** $[Fe,Mn]WO_4$ are tungstates of calcium and of iron and manganese, respectively. By fusion of wolfram with sodium carbonate and extraction with water, **sodium tungstate** $Na_2WO_4,2H_2O$ is secured. It is used as a mordant and for rendering muslin fireproof. Acids precipitate **tungstic acid** H_2WO_4,H_2O from solutions of this salt. The element gives the **oxides** WO_2 and WO_3, the latter being formed by ignition of tungstic acid. The chlorides WCl_2, WCl_4, WCl_5, and WCl_6 are known.

The metal (sp. gr. 19.3) can be liberated by reduction of the oxide by hydrogen or by carbon. It has a higher melting point (3370°) than any other metal and, on this account, and because it is less volatile than carbon, is now used for filaments in electric lamps. A tungsten filament is brighter than one of carbon carrying the same current, and has a much longer life. The powdered metal obtained by reduction is pressed into wire form and then rolled while strongly heated by an electric current until a compact wire is obtained. Shop work has been almost revolutionized by the use of **tungsten steel** tools (see p. 903).

Uranium. — **Pitchblende,** which contains the oxide U_3O_8 along with smaller amounts of many other elements, is found mainly in Joachimsthal (Bohemia) and in Cornwall. **Carnotite,** a uranate and vanadate of potassium $K_2O,2UO_3,V_2O_5,3H_2O$ occurs in Colorado. Pitchblende is roasted with lime, and the calcium uranate $CaUO_4$ thus formed is decomposed with sulphuric acid, giving **uranyl sulphate** UO_2SO_4. When excess of sodium carbonate is added to the solution of the latter, the foreign metals are precipitated and **sodium diuranate** $Na_2U_2O_7,7H_2O$, which is also thrown down, dissolves in the excess as Na_2UO_4.

After filtration, the diuranate of sodium is reprecipitated by neutralizing with sulphuric acid and boiling. This salt is used in making **uranium glass,** which shows a yellowish-green fluorescence. The **oxides** are UO_2 a basic oxide, U_2O_3, U_3O_8 the most stable oxide, UO_3 uranic anhydride, and UO_4 a peroxide.

When the oxide UO_2 is treated with acids, it gives uranous salts such as **uranous sulphate** $U(SO_4)_2,4H_2O$. Uranic anhydride and uranic acid interact with acids, giving basic salts, such as $2UO_2SO_4,$-$7H_2O$, and $UO_2(NO_3)_2,6H_2O$, which are named **uranyl sulphate, uranyl nitrate,** and so forth. They are yellow in color, with green fluorescence. Ammonium sulphide throws down the brown, unstable **uranyl sulphide** UO_2S from their solutions.

The most striking property exhibited by uranium and its compounds, *radioactivity,* has been dealt with in a previous chapter (Chapter XXVI).

MANGANESE Mn

The Chemical Relations of the Element. — Manganese stood, until very recently, alone on the left side of the eighth column of the periodic table. The right side is occupied by the halogens.

In 1925, Noddack and Tacke discovered traces of the two missing elements with atomic numbers 43 and 75, both in platinum ores and in columbite (an ore of columbium, p. 871), by examining the X-ray spectra (Fig. 133, p. 474) of concentrates derived therefrom. These elements have been named **masurium** (symbol Ma) and **rhenium** (symbol Re) respectively.

Masurium compounds have not yet been isolated for study, but rhenium (m.p. over 3000°, sp. gr. 21.2) has been found to yield many compounds analogous to those of manganese (*e.g.,* potassium per-rhenate $KReO_4$). It also resembles osmium (its immediate neighbor in the periodic system) in forming a readily fusible tetroxide ReO_4.

Manganese is never univalent, as are the halogens, but its heptoxide Mn_2O_7 and the corresponding acid, permanganic acid $HMnO_4$, are

in many ways closely related to the heptoxide of chlorine and perchloric acid $HClO_4$. Of the lower oxides of manganese, MnO is basic, and Mn_2O_3 feebly basic. MnO_2 is feebly acidic, MnO_3 more strongly so, and permanganic acid (from Mn_2O_7) is a very active acid. Contrary to the habit of feebly acidic and feebly basic oxides, such as those of zinc, aluminium, and tin, the basic oxides of manganese are not at all acidic, and the acidic oxides, with the exception of MnO_2, are not also basic. There are thus the five following, rather well-defined sets of compounds, showing five different valences of the element. Of these the first, fourth, and fifth are the most stable and most important.

1. **Manganous compounds,** MnO, $Mn(OH)_2$, $MnSO_4$, etc. These compounds resemble those of the magnesium family (and those of Fe^{++}). The salts of weak acids, such as the carbonate and sulphide, are easily made, and there is little hydrolysis of the halides. The salts are pale-pink in color.

2. **Manganic compounds,** Mn_2O_3, $Mn(OH)_3$, $Mn_2(SO_4)_3$, $[MnCl_3]$. The salts resemble the chromic and aluminium salts in behavior, but are even less stable than those of quadrivalent lead. They are completely hydrolyzed by little water. The salts are violet in color.

3. **Manganites,** MnO_2, H_2MnO_3, $CaMnO_3$. The alkali manganites are strongly hydrolyzed, like the plumbates and the stannates. Salts of the type $MnCl_4$ also exist, but are very unstable (see p. 240).

4. **Manganates,** MnO_3, H_2MnO_4, K_2MnO_4. The salts resemble the sulphates and chromates, but are much more easily hydrolyzed. The free acid resembles chloric acid (p. 386) in that, when it decomposes, it yields a higher acid ($HMnO_4$) and a lower oxide (MnO_2). The salts are green in color.

5. **Permanganates,** Mn_2O_7, $HMnO_4$ (hydrated), $KMnO_4$. The salts resemble the perchlorates, and are not hydrolyzed by water. They are reddish-purple in color.

It will be seen that the element manganese changes its character totally with change in valence, and in each form of combination resembles some set of elements of valence identical with that which it has itself assumed. Since the valence represents the number of electrons gained or lost by each atom (p. 148), it is thus evident that the chemical relations of an element depend more upon the electrical constitution of its atom than upon the atomic weight (see p. 498).

Occurrence and Isolation. — The chief ore is the dioxide, **pyrolusite** MnO_2, which always contains compounds of iron. Other

manganese minerals are: **braunite** Mn_2O_3; the hydrated form, **manganite** $MnO(OH)$; **hausmannite** Mn_3O_4; and **manganese spar** $MnCO_3$. The last is isomorphous with calcite. The metal is most easily made by reducing one of the oxides with aluminium by Goldschmidt's method.

Physical and Chemical Properties. — The metal manganese (m.-p. 1260°) has a grayish luster faintly tinged with red. It is oxidized superficially by air, and easily displaces hydrogen from dilute acids, giving manganous salts. Its alloys with iron, such as **spiegel iron** (5–15 per cent Mn) and **ferro-manganese** (70–80 per cent Mn), are made by using manganese ores with the charge in the blast furnace, and are added to the iron in making special steels (see p. 902). Wire, made of an alloy called **manganin** (see p. 694), invented by Weston, is used in instruments for making electrical measurements, because its resistance does not alter with moderate changes in temperature.

Oxides. — **Manganous oxide** MnO is a green powder, made by reducing any of the other oxides with hydrogen. **Hausmannite** Mn_3O_4 is dull red. An oxide having this composition is formed when any of the other oxides is heated in air, oxidation or reduction, as the case may be, taking place (compare p. 831). This oxide corresponds to minium Pb_3O_4 (p. 832) rather than Fe_3O_4 (p. 906), for with dilute acids it gives a soluble manganous salt and a precipitate of the dioxide:

$$Mn_2MnO_4 + 4HNO_3 \rightarrow 2Mn(NO_3)_2 + H_4MnO_4 \downarrow .$$

The hydrated dioxide H_4MnO_4 subsequently loses water. Hausmannite also forms square prismatic crystals. In view of its behavior with acids and its crystalline form, it is considered an orthomanganite of manganese Mn_2MnO_4, rather than a derivative of manganic oxide, $Mn(MnO_2)_2$, which would be a spinelle (p. 772). **Manganic oxide** Mn_2O_3 is brownish-black and is formed by heating any of the oxides in oxygen.

Manganese dioxide MnO_2 is black, and is most easily prepared in pure condition by gentle ignition of manganous nitrate. The hydrated forms of the oxide are produced by reactions like those just mentioned, and by adding a hypochlorite or hypobromite to manganous hydroxide suspended in water. Manganese dioxide is **not** a peroxide (see p. 368); its reaction formula is $O{=}Mn{=}O$. It

was formerly used for manufacturing chlorine, but electrolytic processes have now driven it out of this field. In glass-making (p. 665), it is employed to oxidize the green ferrous silicate, derived from impurities in the sand, to the pale-yellow ferric compound. The amethyst color of the manganic silicate which is formed tends also to neutralize this yellow. The dioxide forms the depolarizer in the Leclanché cell (p. 848). It is mixed with black paints as a "dryer" (oxidizing agent).

Manganese trioxide MnO_3 is a red, unstable powder. **Manganese heptoxide** Mn_2O_7 is a brownish-green, volatile oil (see p. 891).

When any of these oxides is heated with an *acid*, a manganous salt is obtained. Salts of this class are, in fact, the only stable substances in which manganese is combined with an acid radical. In this action the oxides containing more oxygen than does MnO give off oxygen, or oxidize the acid (see p. 240). When the oxides are heated with *bases*, in the presence of air, manganates are always formed. With the oxides containing a smaller proportion of oxygen than MnO_3, oxygen is taken from the air.

Manganous Compounds. — The manganous salts are formed by the action of acids upon the carbonate or any of the oxides. Thus the **chloride** $MnCl_2,4H_2O$ is obtained in pale-pink crystals from a solution made by treating the dioxide with hydrochloric acid and driving off the chlorine liberated by oxidation (p. 240). The **hydroxide** $Mn(OH)_2$ is formed as a white precipitate when a soluble base is added to a solution of a manganous salt. This body passes into solution when ammonium salts are added, and cannot be precipitated when they are present in excess on account of the suppression of the concentration of hydroxyl-ion (compare magnesium hydroxide, p. 743). The hydroxide quickly darkens when exposed to the air and passes over into hydrated manganic oxide $MnO(OH)$.

Manganous sulphate gives pink crystals. Below 6° the aqueous solution deposits $MnSO_4,7H_2O$, which is a vitriol (p. 749). Between 7° and 20° the product is $MnSO_4,5H_2O$, asymmetric and isomorphous with $CuSO_4,5H_2O$. Above 25° monosymmetric prisms of $MnSO_4,4H_2O$ are obtained.

These hydrates have different aqueous tensions and may be formed from one another by lowering or raising the pressure of water vapor around the substance (p. 690). The significance of the temperatures proper to the crystallization of each (compare pp. 208, 689, 726) is that a given solid hydrate can be

formed only from a solution which is saturated with respect to that hydrate and has an aqueous tension *above* that at which the hydrate decomposes to a lower hydrate, and at the same time *below* that at which it combines with water to form a higher hydrate. These conditions are necessary to that state of equilibrium between the solution and the hydrate on which the co-existence of solution and hydrate during crystallization depends (see p. 218). Hence, the hydrates with the larger proportions of water, which are stable at the higher aqueous tensions, are formed in the colder solutions which contain less of the solute when saturated and have therefore at a given temperature themselves relatively high aqueous tensions.

The presence of a foreign dissolved body, since it will lower the vapor tension of the solution, may similarly cause the formation of a lower hydrate. Thus, at the ordinary temperature, calcium sulphate solution has a higher aqueous tension than gypsum, and therefore gypsum is deposited from it, and anhydrite will turn into gypsum if placed in it. But calcium sulphate solution containing much of the chlorides of sodium and magnesium has a lower aqueous tension than gypsum, and so anhydrite is deposited, and gypsum in contact with such a solution would lose its water of hydration. This explains the deposition of anhydrite in the salt layers (see p. 698). Similarly, gradual additions of sulphuric acid to a saturated copper sulphate solution at room temperatures, where the pentahydrate $CuSO_4,5H_2O$ is ordinarily stable, give first the trihydrate, then the monohydrate, and finally the anhydrous salt as the stable solid phase.

Manganous carbonate $MnCO_3$ is a white powder formed by precipitation. The **sulphide** MnS is obtained as a green, crystalline powder by leading hydrogen sulphide over any of the oxides. A flesh-colored, amorphous variety MnS (often somewhat hydrated) is more familiar and is precipitated by ammonium sulphide from manganous salts. It interacts with active acids and even with acetic acid, so that it cannot be precipitated by hydrogen sulphide (compare p. 750). When rubbed in a mortar it becomes crystalline, and is then green.

The manganous salts of weak acids, such as the carbonate and sulphate, darken when exposed to air and are oxidized, with formation of hydrated manganic oxide. As we have seen, manganous hydroxide is similarly oxidized and these salts are precisely the ones which should furnish the hydroxide by hydrolysis. While there is a general resemblance between the manganous salts and the stannous, chromous, and ferrous salts, the manganous salts of active acids are not oxidized by the air as are the corresponding salts of the other three metals.

Manganic Compounds. — The base of this set of compounds, **manganic hydroxide** $Mn(OH)_3$, is slowly deposited by the action of the air on an ammoniacal solution of a manganous salt in salts of

ammonium. The **chloride** $MnCl_3$ is present in the liquid obtained by the action of hydrochloric acid upon manganese dioxide (see p. 240), but loses chlorine very readily and cannot be isolated. Double salts, however, such as $MnCl_3,2KCl$ and $MnF_3,2KF,2H_2O$, are known. **Manganic sulphate** $Mn_2(SO_4)_3$ is deposited as a violet-red powder when hydrated manganese dioxide is heated with concentrated sulphuric acid at 160°. It is deliquescent and is rapidly hydrolyzed in the cold even by a little water, giving the brownish-black hydroxide:

$$Mn_2(SO_4)_3 + 6H_2O \rightarrow 2Mn(OH)_3 + 3H_2SO_4.$$

The **caesium-manganic alum** $Cs_2SO_4,Mn_2(SO_4)_3,24H_2O$ seems to be the most stable derivative.

Manganites. — Although manganese dioxide interacts when fused with potassium hydroxide, simple salts derived from H_2MnO_3 ($= H_2O,MnO_2$) or H_4MnO_4 ($= 2H_2O,MnO_2$) are not formed. The products are complex, as $K_2Mn_5O_{11}$. Some less complex manganites are formed in the **Weldon process** for regenerating manganese dioxide from the manganous chloride, formerly obtained in manufacturing chlorine by the method described on p. 240. The liquor is mixed with slaked lime, and air is blown through the mass of calcium and manganous hydroxides which is obtained. Black manganates of calcium, such as $CaMnO_3$ ($= CaO,MnO_2$) and $CaMn_2O_5$ ($CaO,2MnO_2$) are thus formed:

$$Ca(OH)_2 + 2Mn(OH)_2 + O_2 \rightarrow CaMn_2O_5 + 3H_2O,$$

and when afterwards treated with hydrochloric acid this "Weldon mud" behaves like a mixture of manganese dioxide and calcium oxide, so that the same material may be used over and over again.

Manganates. — When one of the oxides of manganese is fused with potassium carbonate (or other alkali) and potassium nitrate (or other oxidizing agent) a green mass is obtained. The green aqueous extract deposits **potassium manganate** K_2MnO_4 in rhombic crystals, which are isomorphous with those of potassium sulphate, and are almost black:

$$2K_2CO_3 + 2MnO_2 + O_2 \rightarrow 2K_2MnO_4 + 2CO_2.$$

The acid H_2MnO_4, itself unknown, must be weak, for the potassium salt is easily hydrolyzed. The salt remains unchanged in solution

only in presence of free alkali, the hydroyxl-ion of the alkali combining with and suppressing the hydrogen-ion of the water whose combination with the $MnO_4^{=}$ ion constitutes the hydrolysis. When the concentration of the hydroxyl-ion is reduced by dilution, or, better still, when a weak acid such as carbonic acid or acetic acid is used to neutralize it, the salt is decomposed according to the following equation:

$$3K_2MnO_4 + 2H_2O \rightarrow 4KOH + 2KMnO_4 + MnO_2.$$

That is, a precipitate of manganese dioxide and a solution of potassium permanganate are obtained. In terms of the ions (see p. 379) the equation is simpler:

$$3MnO_4^{=} + 2H^+ \rightarrow 2OH^- + 2MnO_4^- + MnO_2.$$

The alkaline solution of potassium manganate interacts readily with oxidizable substances. Thus oxalic acid is converted into carbonic acid, and alcohol into acetic acid. The details of the change depend upon the amount of free alkali present and the nature of the product of oxidation. Lower oxides of manganese such as MnO_2 are usually precipitated.

Permanganates. — **Potassium permanganate** $KMnO_4$ is made by hydrolysis of the manganate as shown above, and is obtained, as purple crystals with a greenish luster, by evaporation of the solution. The crystals are rhombic prisms, isomorphous with potassium perchlorate. To avoid the loss of manganese thrown down as dioxide, the action is carried out commercially either by passing chlorine through the solution of the manganate:

$$2K_2MnO_4 + Cl_2 \rightarrow 2KMnO_4 + 2KCl,$$

or by electrolytic oxidation, the reaction at the anode being represented by the equation:

$$MnO_4^{=} \rightarrow MnO_4^- + \ominus.$$

Sodium permanganate $NaMnO_4$ is made in a similar manner. Aluminium permanganate in solution is sold as "Condy's disinfecting fluid." This liquid owes its properties to the oxidizing power of the permanganic acid, formed by hydrolysis of the salt. **Permanganic acid** is a very active acid, that is, it is highly ionized in aqueous

solution. A solid hydrate of the acid may be secured in reddish-brown crystals by adding sulphuric acid to a solution of barium permanganate and allowing the filtrate to evaporate:

$$Ba(MnO_4)_2 + H_2SO_4 + xH_2O \rightleftarrows BaSO_4 \downarrow + 2HMnO_4,xH_2O.$$

This hydrate decomposes, on being warmed to 32°, and yields oxygen and manganese dioxide.

When a very little dry, powdered potassium permanganate is moistened with concentrated sulphuric acid, brownish-green, oily drops of **permanganic anhydride** (manganese heptoxide) Mn_2O_7 are formed. This compound is volatile, giving a violet vapor, and is apt to decompose explosively into oxygen and manganese dioxide. Its oxidizing power is such that combustibles like paper, ether, and illuminating gas are set on fire by contact with it.

Potassium Permanganate as an Oxidizing Agent. — The actions are different according as the substance is employed (1) in alkaline or (2) in acid solution.

1. When an alkali, such as potassium hydroxide, is added, the action by which the permanganate is formed is reversed, and the solution becomes green from the production of the **manganate:**

$$4KMnO_4 + 4KOH \rightarrow 4K_2MnO_4 + 2H_2O + O_2,$$

or

$$4MnO_4^- + 4OH^- \rightarrow 4MnO_4^= + 2H_2O + O_2.$$

When a substance capable of being oxidized is present, the reduction proceeds further and manganese dioxide is precipitated.

2. In presence of an acid, and an oxidizable body, a **manganous** salt is always formed. An example of this type (the oxidation of hydrochloric acid to chlorine) has already been discussed in detail (pp. 239, 379).

The quantity of a ferrous salt in a sample of a solution may be measured by titrating (p. 337) the solution with a standard solution of potassium permanganate until the color ceases to be destroyed, and then noting the volume used. For convenience, the standard solution may be prepared so that 1 c.c. will oxidize 0.01 g. of Fe^{++}. The quantitative analysis of a solution of hydrogen peroxide may readily be made in a similar way (see p. 370).

When **dry** potassium permanganate is heated, it decomposes as follows:

$$2KMnO_4 \rightarrow K_2MnO_4 + MnO_2 + O_2.$$

The fingers are stained brown by an aqueous solution, receiving a deposit of manganese dioxide, in consequence of the reducing power of the unstable organic substances in the skin. The destruction of minute organisms by Condy's fluid results from a similar action. When the powdered salt is moistened with glycerine, the mass presently bursts into flame.

Analytical Reactions of Manganese Compounds. — The ions commonly encountered are manganous-ion Mn^{++}, which is very pale-pink in color, permanganate-ion MnO_4^-, which is purple, and manganate-ion $MnO_4^{=}$, which is green. The manganous compounds give with ammonium sulphide the flesh-colored sulphide, which is soluble in acids. Bases give the white hydroxide, which darkens by oxidation, and is soluble in salts of ammonium. All compounds of manganese confer upon the borax bead an amethyst color (manganic borate), which, in the reducing flame, disappears (manganous borate). A bead of sodium carbonate and niter becomes green on account of the formation of the manganate.

Exercises. — 1. What do we mean by saying that, (*a*) chromous chloride is stable (p. 173), but easily oxidized by the air, (*b*) permanganic acid is an active oxidizing agent in presence of an acid?

2. Formulate the oxidations of hydrogen sulphide, of ferrous sulphate, of oxalic acid $H_2C_2O_4$ (to carbon dioxide), and of nitrous acid (to nitric acid) by potassium permanganate in acid solution. In doing so, employ the two methods suggested on pp. 378–9.

3. Construct equations, showing the interactions of: (*a*) chromic oxide and aluminium, (*b*) strontium nitrate and potassium dichromate in solution, (*c*) potassium hydroxide and chromic hydroxide, and the reversal on boiling, (*d*) chlorine and potassium chromite in excess of alkali (what is the actual oxidizing agent?).

4. What volume of oxygen at 0° and 760 mm., (*a*) is obtainable from one formula-weight of potassium dichromate, (*b*) is required to oxidize one formula-weight of chromous chloride?

5. Make equations for all the reactions involved in the preparation of sodium diuranate from pitchblende.

6. What weight of potassium dichromate will be obtained from 100 kg. of chromite (p. 874), assuming that the chromite is 80% pure and that the conversion process is only 90% efficient?

7. Balance the following equations by the ion and electron method:

(*a*) $Fe(CrO_2)_2 + K_2CO_3 + O_2 \rightarrow Fe_2O_3 + K_2CrO_4 + CO_2$
(*b*) $K_2Cr_2O_7 + H_2SO_4 + H_2SO_3 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + H_2O$
(*c*) $K_2Cr_2O_7 + S \rightarrow K_2SO_4 + Cr_2O_3$
(*d*) $CrCl_2 + HCl + O_2 \rightarrow CrCl_3 + H_2O$.

8. Solutions of chromic chloride and potassium chromate, in equivalent proportions, are mixed. What is the result? Explain.

9. Starting with potassium dichromate in each case, how would you proceed to prepare: (*a*) potassium chromate, (*b*) silver chromate, (*c*) chromic anhydride, (*d*) chromic chloride, (*e*) chromic oxide, (*f*) potassium chromite, (*g*) chromous chloride, (*h*) metallic chromium? Give complete equations.

10. In what respects is potassium dichromate analogous to potassium pyrosulphate, and in what respects does it differ? Give equations. Would it be correct to call potassium dichromate by any of the following names: potassium bichromate, potassium pyrochromate, potassium acid chromate? Justify your answer in each case.

11. Explain in detail why addition of ammonium sulphide to chromic sulphate solution gives a precipitate of chromic hydroxide instead of chromic sulphide.

12. In what respects does manganous hydroxide resemble magnesium hydroxide, and in what respects does it differ? Give equations.

13. In what respects do manganic salts resemble chromic salts, and in what respects do they differ? Give equations.

14. In what respects does potassium manganate resemble potassium chromate, and in what respects does it differ? Give equations.

15. In what respects does potassium permanganate resemble potassium perchlorate, and in what respects does it differ? Give equations.

16. Predict the chief physical and chemical properties of masurium and rhenium (p. 884).

17. Balance the following equations by the ion and electron method:

(*a*) $Ca(OH)_2 + Mn(OH)_2 + O_2 \rightarrow CaMn_2O_5 + 3H_2O$
(*b*) $MnO_2 + FeSiO_3 + SiO_2 \rightarrow Mn_2(SiO_3)_3 + Fe_2(SiO_3)_3$
(*c*) $KMnO_4 + KOH \rightarrow K_2MnO_4 + H_2O + O_2$.

18. Solutions of manganous chloride and potassium permanganate, in equivalent proportions, are mixed. What is the result? Explain.

19. Starting with potassium permanganate, in each case, how would you proceed to prepare: (*a*) potassium manganate, (*b*) potassium manganite, (*c*) manganese dioxide, (*d*) manganic hydroxide, (e) manganous chloride, (*f*) manganese? Give complete equations.

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CHAPTER LII

IRON, COBALT AND NICKEL

The elements **iron** (Fe, atomic number 26), **cobalt** (Co, at. no. 27), and **nickel** (Ni, at. no. 28) are not corresponding members of successive periods, like most of the families hitherto considered. They are neighboring members of the first long period, lying between its two octaves (p. 446), and form a transition group between the adjoining elements within those octaves (compare p. 815). Thus, iron forms ferrates $M_2{}^{I}Fe^{VI}O_4$ and ferric salts $Fe^{III}Cl_3$, as well as ferrous salts $Fe^{II}Cl_2$. These resemble chromates and manganates, chromic and manganic salts, and chromous and manganous salts, respectively. Cobalt forms cobaltic and cobaltous salts, like $Co_2{}^{III}(SO_4)_3$ and $Co^{II}Cl_2$. Nickel enters only into nickelous salts, like $NiCl_2$, and thus links iron and cobalt with copper and zinc, which are both bivalent elements. In this connection, the various electron arrangements in the atoms of the three elements under consideration, occasioned by the sliding of electrons from the outermost shell to an unfilled inner one, should be studied, and similarities with the electron arrangements exhibited by atoms of resembling elements carefully noted (see p. 498).

The free metals of this family are magnetic, iron showing this property strongly and cobalt very distinctly.

Iron Fe

Chemical Relations of the Element. — The oxides and hydroxides FeO and $Fe(OH)_2$, Fe_2O_3 and $Fe(OH)_3$ are basic, the former more strongly so than the latter. The ferrous salts, derived from $Fe(OH)_2$, resemble those of the magnesium group and those of Cr^{++} and Mn^{++} and are little hydrolyzed. The ferric salts, derived from $Fe(OH)_3$, resemble those of Cr^{+++} and Al^{+++} and are noticeably hydrolyzed. Ferric hydroxide is even less acidic, however, than is chromic hydroxide. Iron gives also a few ferrates

K_2FeO_4, $CaFeO_4$, etc., derived from an acid H_2FeO_4 which, like manganic acid H_2MnO_4 (p. 889), is too unstable to be isolated. Complex anions containing this element, such as the anion of $K_4.Fe(CN)_6$, are familiar, but complex cations containing ammonia (see p. 748) are unknown.

The ferrous salts differ from most of the manganous salts and resemble the chromous and stannous salts in being easily (although not quite so easily) oxidized by the air, passing into the ferric condition.

Occurrence. — Free iron is found in minute particles in some basalts, and many **meteorites** are composed of it. Meteoric iron can be distinguished from specimens of terrestrial origin by the fact that it contains 3–8 per cent of nickel. The chief ores of iron are the oxides, **hæmatite** Fe_2O_3 and **magnetite** Fe_3O_4, and the carbonate $FeCO_3$, **siderite.** The first is reddish and columnar in structure; but black, shining, rhombohedral crystals, known as **specularite,** are also found. Hydrated forms, like **brown iron ore** $2Fe_2O_3,3H_2O$, are also common. Siderite is pale-brown in color and rhombohedral, isomorphous with calcite. When mixed with clay it forms **ironstone** and, with 20–25 per cent of coal in addition, **black-band.** Most of the iron in Great Britain, but less than one per cent of that in the United States, is obtained from these two sources. **Pyrite** FeS_2 consists of golden-yellow, shining cubes or pentagonal dodecahedra. It is used, on account of its sulphur, in the manufacture of sulphuric acid, but, from the oxidized residue, iron of sufficient purity is obtained with difficulty. Compounds of iron are found in the blood (**hæmoglobin** is built up from a protein, *globin,* and *hæmatin,* which contains iron), and doubtless play an important part in connection with the vital functions. By interaction with organic compounds of iron present in the tissues, ammonium sulphide blackens the skin, ferrous sulphide being formed.

Metallurgy. The Blast Furnace. — The ores of iron are first roasted in order to decompose carbonates and oxidize sulphides, if these salts are present. Coke is then used to reduce the oxides in the blast furnace. The carbon monoxide CO, produced by the burning of the coke and air, is the actual reducing agent:

$$Fe_3O_4 + CO \rightleftarrows 3FeO + CO_2.$$
$$FeO + CO \rightleftarrows Fe + CO_2.$$

Coal is unsuitable because so much heat is wasted in driving out the volatile matter and moisture, which are absent from coke. Ores containing lime or magnesia are mixed with an acid flux, such as sand or clay-slate, in order that a fusible slag may be formed. Conversely, ores containing silica and clay are mixed with limestone.

The blast furnace (Fig. 218) is an iron structure 40 to 100 feet high, lined with fire-brick. A circular pipe delivers a blast of preheated compressed air to several nozzles *T* (tuyères) near the foot. The ore, coke and limestone are admitted at the top. Reduction of the ore occurs continuously as the solid materials, passing downwards, become hotter and hotter through combustion of the coke. The melted iron and slag (immiscible) finally collect in two layers in the hearth or crucible at the bottom. From time to time the slag is allowed to flow from an opening near the top of the crucible, and the iron from a similar opening at the bottom. Plugs of wet clay close the openings and are instantly baked hard. The iron is taken in ladles to other parts of the plant, or is cast into "pigs" in steel molds and chilled in water.

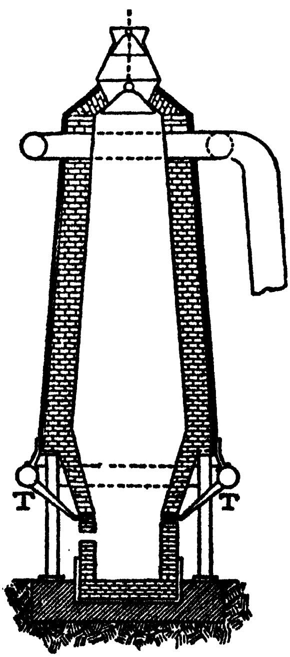


FIG. 218. Blast Furnace.

Reactions in the Blast Furnace. — The actions (see equations on p. 895) are both *reversible* and the carbon dioxide formed tends to react to reproduce the original materials. At any particular temperature it is necessary therefore to keep the proportion of CO_2 to CO in the furnace gases below a certain value in order to prevent the reversal of the reactions. This proportion of CO_2 to CO is regulated, however, by a third reversible reaction:

$$C + CO_2 \rightleftarrows 2CO.$$

At high temperatures (above 1000°) this reaction is almost complete in the forward direction. As the temperature falls, the proportion of CO_2 in the equilibrium mixture increases rapidly.

If all three reactions had time to attain equilibrium conditions in the blast furnace, reduction of Fe_3O_4 to FeO, and of FeO to Fe, would occur at about 645° and 700° respectively, and the residual gases would contain very little CO. In practice, however, the slowness of the reactions necessitates the use of much higher temperatures and a large excess of CO. The gases that escape are therefore *combustible*, and are led off through openings near the top of the furnace and used for pre-heating the air-blast.

In 1935, nearly 22,000,000 tons of **pig iron** were produced in the United States. The production in Great Britain exceeded 6,500,000 tons. These figures are much lower than the normal, owing to trade depression. The maximum world's output, 98,000,000 tons, was in 1929.

Cast Iron. — Pure iron is not manufactured, and indeed would be too soft for most purposes. Piano-wire, however, is about 99.7 per cent pure. The product obtained from the blast furnace contains 92–94 per cent of iron along with 2.6–4.3 per cent of carbon, often nearly as much silicon, varying proportions of manganese, and some phosphorus and sulphur. Pig iron does not soften before melting, but melts sharply at 1150°–1250° according to the amount of foreign material it contains. When castings made from it are *suddenly* cooled we obtain **white cast iron,** all the carbon of which is present in the form of carbide of iron Fe_3C (cementite) in solid solution in the metal. This solid solution is exceedingly *hard,* but very *brittle.* By slower cooling, opportunity is permitted for the separation of part of the carbon as graphite, which appears in tiny black scales, and **gray cast iron** *results.* This mixture is much *softer* and less *brittle,* on account of the amount of free, relatively pure iron which it contains.

Cast iron is **used** in making cooking ranges, stoves, pipes, and radiators. It expands in solidifying, and so fills every detail of the mold.

Wrought Iron. — Wrought iron is made by heating the broken pigs of cast iron upon a layer of material containing oxide of iron and hammer-slag (basic silicate of iron) spread on the bed of a **reverberatory furnace** (Fig. 219). The flames and heated gases coming over from the furnace *A,* deflected by the low roof, play directly upon the iron in the bed *B* and melt it. The carbon, silicon, and phosphorus combine with the oxygen of the oxide, and

the last two pass into the slag. Spiegel-iron (5–15 per cent Mn, see p. 886) is added in sufficient quantity to cause the sulphur also to pass into the slag in the form of manganese sulphide. On account of the effervescence due to the escape of carbon monoxide, the process is called "pig-boiling." The iron is stirred with iron rods ("puddled") and stiffens as it becomes purer, until finally it can be withdrawn in balls ("blooms") and partially freed from slag by rolling. The resulting bars are repeatedly cut, piled in a bundle, reheated, and rolled. The iron now softens sufficiently for welding below 1000° and melts at 1530°. If it still contains more than a trace of combined phosphorus it is brittle when cold ("cold-short"). A little surviving sulphide of iron makes it brittle when hot ("red-short") and unsuitable for forging.

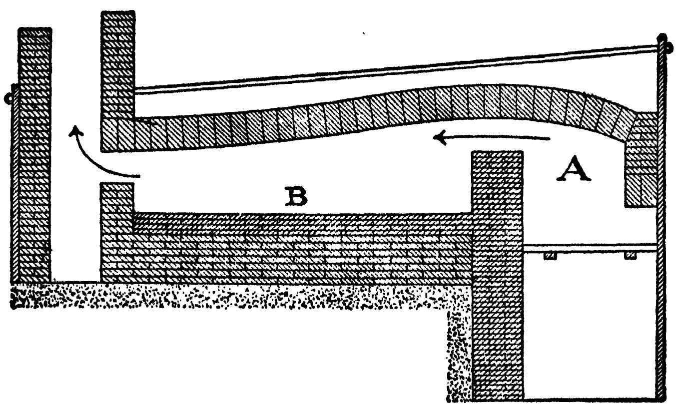


FIG. 219. Reverberatory Furnace.

Wrought iron should contain only 0.1–0.2 per cent of carbon. Its *fibrous structure* is due partly to the films of slag which have not been completely pressed out by the rolling. On account of its *toughness*, wrought iron is used for anchors, chains, and bolts, and for drawing into wire. On account of its *relative purity* (99.8–99.9 per cent), it is less fusible than cast iron and is used for fire bars.

Steel. — This is a variety of iron almost free from phosphorus, sulphur, and silicon, but richer in carbon than wrought iron. Tool-steel contains 0.9–1.5 per cent of carbon, machine steels only 0.2–0.6 per cent, and mild steel 0.2 per cent or even less. Steel combines the properties of cast and of wrought iron, being *hard* and

elastic, and at the same time available for forging and welding when the proportion of carbon is not too high. Steel can be *tempered* (see p. 901). It has also a greater *tensile strength* (see p. 679) than has wrought iron, and it can be *permanently magnetized.*

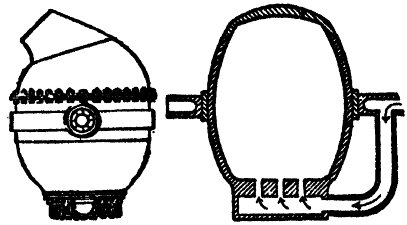


FIG. 220. Bessemer Converter (two views).

Bessemer Process. — Steel is made largely in Europe by the Bessemer process. The molten cast iron is poured into a converter (Fig. 220), lined with sand and clay, and a blast of air is blown through it from tuyères at the bottom. The oxidation of the manganese, carbon, silicon, and a little of the iron gives out sufficient heat to raise the temperature of the mass above the melting-point of wrought iron. The required proportion of carbon is then introduced by adding pure cast iron, spiegel iron (p. 886), or coke, and the contents, first the slag and then the molten steel, are finally poured out by turning the converter. When the cast iron contains much phosphorus, the oxide of this element is reduced again by the iron as fast as it is formed by the blast. In such cases a basic lining containing lime and magnesia takes the place of the sand and clay lining of the ordinary Bessemer converter, and a slag containing a basic phosphate of calcium is produced. This modification constitutes what is known as the basic or Thomas-Gilchrist process. The slag ("Thomas-slag") when pulverized forms a valuable fertilizer (see also p. 779).

Bessemer steel is used for heavy and light machinery castings, and is rolled into bridge and structural iron. It contains from 0.1 per cent (soft) to 1 per cent (hard) of carbon. In the United States, the basic open-hearth process is preferred.

Open-Hearth (Siemens-Martin) Process. — In this process the cast iron is melted in a saucer-shaped depression (Fig. 221), which is lined with sand in the acid process and with lime and magnesia in the basic process. Scraps of steel plate (for dilution) and hæmatite, or some other oxide ore, are then added in proper proportions. The materials (100–200 tons in one charge) are heated with gas fuel for 11–15 hours. To secure economically the high temperature required to keep the product (almost pure iron) fused, Siemens de-

vised the method of preheating the fuel gas and air by a regenerative device. The spent air and gas pass down through a checkerwork of brick. When this becomes heated, the valves are reversed, the gas and air now enter through the heated brickwork and, after meeting and burning over the iron, pass out through the checkerwork on the opposite side, raising its temperature in turn.

The changes are similar to those in the Bessemer process. During casting, some aluminium is added to combine with oxygen (present as CO) and give sounder ingots. Recently, iron containing a small amount of **titanium** has been added instead. The titanium combines with both nitrogen and oxygen and the compounds

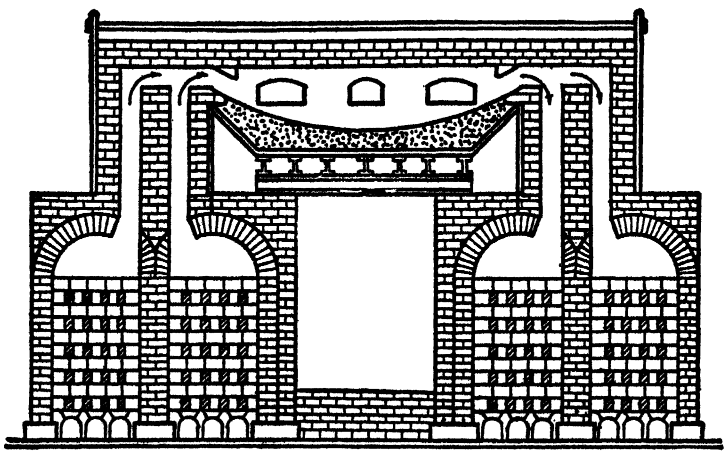


FIG. 221. Open-Hearth Furnace.

pass into the slag, just as does aluminium oxide. Rails made of steel purified with this element are less liable to breakage (the commonest cause of wrecks) and are also considered to be more durable than are ordinary open-hearth rails.

Open-hearth steel is used for the better class of rails, for railway bridges, and wherever the steel is subject to much vibration.

Crucible Steel. — For special purposes steel is occasionally made in crucibles of clay (or graphite and clay) in melts of 60–100 pounds. "Melting bar," a very pure open-hearth steel, is re-melted with charcoal or with pure pig iron. Crucible steel is employed in making razors (1.5 per cent C), tools (1 per cent C), dies (0.75 per cent C), pens, needles, and cutlery.

Electric Steel. — The electric furnace permits more careful adjustment of conditions in steel manufacture than is possible with any other process, and it is accordingly used to obtain products where extreme dependability is essential, such as engines, axles and wheels. In the electric furnace, oxidation and reduction can be carried to any point desired, the temperature can be controlled within a very few degrees, and the two most objectionable impurities always present in steel — sulphur and phosphorus — can be eliminated down to the merest trace. Compared with steel made by any other method, electric steel is denser, is free from blowholes, occluded gases and slag, and is stronger, tougher and more ductile. The temperature readily obtainable is also greater than in the older processes, so that the treatment of specially infusible alloys is facilitated and the time of operation shortened.

Many products formerly made by the open-hearth process, such as shafts, armor plate, and heavy guns, are now more generally manufactured with the aid of the electric furnace.

The total production of steel in the United States in 1935 was 34,092,594 gross tons, of which 30,715,429 tons were open-hearth, 2,835,031 tons Bessemer, 541,492 tons electric steel, and 642 tons crucible steel.

Tempering. — When steel is heated to redness and cooled slowly, it is comparatively soft. Sudden chilling, however, renders it harder than glass. By subsequent, cautious heating the hardness may be reduced to any required extent, and this treatment is called **tempering.** The sufficiency of the heating is judged roughly by the interference colors caused by the thin film of oxide which forms on the surface. Thus a pale-yellow color (200–220°) serves for tempering razors, a decided yellow (240°) for pen-knives, a brown (260°) for shears, a purple (275°) for table-knives, a blue (300–315°) for watch-springs and sword-blades, and a black-blue (340°) for saws. Except in the case of watch-springs, these films are afterwards removed by the grinding.

To understand the tempering of steel, it must be noted that iron exists in three distinct crystalline modifications which are called α-ferrite, γ-ferrite and δ-ferrite respectively. Each of these is the stable state through a certain temperature range, and definite transition points mark the equilibrium conditions between the various allotropic forms (compare sulphur, p. 400). The form stable below 900° is α-ferrite (wrought iron). It is magnetic, and is shown by X-ray examination to possess a cube-centered cubic space lattice. Between 760° and 900° α-ferrite *gradually* loses its magnetic properties, but otherwise

remains unchanged. The non-magnetic product was formerly thought to be a distinct allotropic modification of iron (β-ferrite) but no definite transition point can be established and X-ray study shows no change in crystal structure. At 900°, however, there is an undoubted change of phase, with absorption of heat, into γ-ferrite, which possesses a face-centered cubic space lattice. At 1400°, again, this is converted into δ-ferrite, and at 1535° this melts.

Now molten iron dissolves carbon readily, and the carbon exists in solution partly in the free state and partly as a carbide of iron, Fe_3C, called **cementite.** When white-hot steel (up to 2 per cent C) is *suddenly chilled,* there is no time for any precipitation to occur during the cooling, and a *supersaturated solid solution* of carbon in α-ferrite is obtained (**martensitic steel**) which is very hard and brittle (see p. 693). When, however, the cooling is slow, so that equilibrium conditions are maintained throughout, the carbon which was in solution at higher temperatures is precipitated as thin plates of cementite alternating with plates of α-ferrite, the product being known as **pearlitic steel** from its pearly appearance when viewed under the microscope. The soft iron which predominates in pearlite makes it relatively soft and ductile. Heating to a high temperature, with sudden chilling, gives the homogeneous solid solution of carbon in α-ferrite once more and restores the qualities characteristic of martensite. Moderated reheating (tempering of the chilled mass), on the other hand, results in more or less partial accomplishment of the changes proper to slow cooling, and consequently in a more or less close approach to the condition which results from this. In tempering, the extent to which the softer material is formed depends on the temperature reached, and on the rate and duration of the cooling permitted. By varying these the degree of hardness allowed to remain can be adjusted just as desired.

The presence of other elements in the steel also exerts a considerable influence on the rapidity with which equilibrium conditions are attained. The complete suppression of all transformations on cooling is especially favored by the addition of manganese and nickel, the resultant product (a solid solution of carbon in γ-ferrite) being known as **austenitic steel.** Silicon acts in the opposite sense, and when present in sufficient quantity prevents the formation of austenite under any circumstances.

Steel Alloys.—We must distinguish between manganese, aluminium, silicon, or titanium added in small amounts (**medicines** or **scavengers**) to purify the iron, and passing (in combination) into the slag, as described on pp. 898, 900, and the present subject, which concerns *metals added* so as to produce *regular alloys.*

Manganese steel (7 to 20 per cent Mn) acquires, by the cold working effect of friction, an exceedingly hard surface, but the core remains soft and ductile. It is used for the jaws of rock-crushing machinery and for burglar-proof safes.

Chromium-vanadium steel (1 per cent Cr, 0.15 per cent V) has great tensile strength, can be bent double while cold, and offers great resistance to changes of stress, and to torsion. It is used for frames and axles of automobiles, and for connecting rods. Steels containing 12 per cent of Cr are highly resistant to corrosion.

Tungsten steel (tungsten 8 to 20 per cent, and chromium 3 to 5 per cent) is used for tools in high-speed metal turning, as it can become red hot (from friction) without loss of temper.

Nickel steel (containing 2 to 4 per cent of nickel) has a very high limit of elasticity and great hardness. It is used for armor-plate, wire cables, and propeller shafts. The alloy with 36 per cent nickel, called **invar,** is practically non-expansive when heated and is valuable for meter-scales and pendulum rods.

Duriron or **tantiron** (15 per cent Si; a cast iron alloy) is rustproof and is not attacked by sulphuric, nitric or acetic acid, hot or cold, dilute or concentrated. Vessels made of this alloy are therefore used industrially in acid concentration.

Chemical Properties of Iron. — Although the purest iron does not rust in cold water, ordinary iron rusts in moist air (p. 13), or under water. Corrosion takes place extremely slowly in water free from carbon dioxide, but the action is greatly hastened by the presence of carbonic acid. Rust is a brittle, porous, loosely adherent coating of variable composition, consisting mainly of a hydrated ferric oxide $3Fe_2O_3,H_2O$, which does not protect the metal below.

Iron *burns* in oxygen, and *acts* when heated *upon steam,* in both cases producing magnetic oxide of iron Fe_3O_4 (p. 95). A thin film of this oxide is adherent, and protects the iron (**Russia iron**). Watch hands, buckles and the like may be given a protective coating by dipping them in an oxidizing bath such as melted saltpeter. Another method of rust-proofing is to immerse iron articles in a hot solution of *ferrous phosphate.* This salt is appreciably hydrolyzed in solution, and the free acid acting upon the iron converts its surfaces into an adherent film of basic phosphate.

Iron displaces hydrogen easily from dilute acids. Steel and cast iron, which contain iron, its carbide, and graphite, give with cold dilute acids almost pure hydrogen, and the carbide and graphite remain unattacked. More concentrated acids, however, particularly when warm, generate, along with hydrogen, hydrocarbons formed by interaction with the carbide (p. 580). The odor of the resulting gas is due to compounds of sulphur and phosphorus.

Although iron acts vigorously on dilute or concentrated nitric acid, it is indifferent to fuming nitric acid (NO_2 in solution, p. 522). It becomes **passive.** In this state, it no longer displaces hydrogen from dilute acids. If

dipped in cupric sulphate solution, it does not receive the usual red coating of metallic copper. However, if the metal is scratched or struck, the passive condition is destroyed, and copper begins to be deposited at the point touched and the action spreads quickly over the whole surface. No satisfactory explanation of this phenomenon has been obtained, although it is shown also by chromium, cobalt, and other metals.

Ferrous Compounds. — Ferrous chloride is obtained as a pale-blue hydrate $FeCl_2,4H_2O$ (turning green in the air) by interaction of hydrochloric acid with the metal or the carbonate. The anhydrous salt sublimes in colorless crystals when hydrogen chloride is led over the heated metal. In solution the salt is oxidized by the air to a basic ferric chloride:

$$4Fe^{++} + O_2 + 2H_2O \rightarrow 4Fe^{+++} + 4OH^-.$$

In presence of excess of the acid, normal ferric chloride is formed. With nitric acid, ferric chloride and nitric oxide are produced (p. 523).

Ferrous hydroxide $Fe(OH)_2$ is thrown down, on addition of bases to solutions of pure ferrous salts, originally as a white precipitate, but rapidly becomes dirty-green and finally brown, by oxidation. It dissolves in solutions of salts of ammonium, being like magnesium hydroxide (p. 743), sufficiently soluble in water to require an appreciable concentration of OH^- for its precipitation. **Ferrous oxide** FeO is black, and is formed by cautious reduction of ferric oxide by hydrogen (at about 300°). It catches fire spontaneously when exposed to the air.

Ferrous carbonate $FeCO_3$ is found in nature as siderite, and may be made in slightly hydrolyzed form by precipitation. The precipitate is white, but rapidly darkens and finally becomes brown, the ferrous hydroxide produced by hydrolysis being oxidized to the ferric condition. The salt interacts with water containing carbonic acid, after the manner of calcium carbonate, giving $Fe(HCO_3)_2$ (p. 729), and hence is found in solution in natural (chalybeate) waters.

Ferrous sulphide FeS may be formed as a black, metallic-looking mass by heating together the free elements (p. 22). It is produced by precipitation with ammonium sulphide, but not with hydrogen sulphide. It interacts readily with dilute acids.

Ferrous sulphate is obtained by allowing pyrite to oxidize in the air and leaching the residue:

$$2FeS_2 + 7O_2 + 2H_2O \rightarrow 2FeSO_4 + 2H_2SO_4.$$

The liquor is treated with scrap iron and the neutral solution evaporated until a hydrate $FeSO_4,7H_2O$, green vitriol, or "copperas," is deposited. The crystals are efflorescent, and become also brown from surface oxidation to a basic ferric sulphate:

$$4FeSO_4 + O_2 + 2H_2O \rightarrow 4Fe(OH)SO_4.$$

With excess of sulphuric acid and air, or an oxidizing agent such as nitric acid, ferric sulphate is formed. The ferrous sulphate is used in dyeing, in making **writing-ink** (see p. 909) and rouge (p. 906), and in the purification of water (p. 776).

The **double salts** of the form $(NH_4)_2SO_4,FeSO_4,6H_2O$ (Mohr's salt) are not efflorescent, and in solid form are less readily oxidized than is ferrous sulphate.

Ferric Compounds.—By leading chlorine into a solution of ferrous chloride, and evaporating until the proper proportion of water alone remains, a yellow, deliquescent **hexahydrate of ferric chloride,** $FeCl_3,6H_2O$ is obtained. When this is heated still further, hydrolysis takes place and the oxide remains. When chlorine is passed over heated iron, **anhydrous** ferric chloride sublimes in dark green scales, which are red by transmitted light. In solution, the salt, like other ferric salts, can be reduced to the ferrous condition by boiling with iron. The same reduction is effected by hydrogen sulphide and by stannous chloride (compare p. 824):

$$2Fe^{+++} + Fe \rightarrow 3Fe^{++}.$$
$$2Fe^{+++} + S^{=} \rightarrow 2Fe^{++} + S\downarrow.$$
$$2Fe^{+++} + Sn^{++} \rightarrow 2Fe^{++} + Sn^{++++}.$$

The last action shows that ferrous salts are less active reducing agents than are the stannous salts.

The ferric ion is almost colorless, the yellow-brown color of solutions of ferric chloride being due to the presence of ferric hydroxide produced by hydrolysis. The color deepens when the solution is heated (increased hydrolysis), and fades again very slowly, by reversal of the action, when the cold solution is allowed to stand. On the other hand, the hydrolysis may be reversed and the color may be almost destroyed, particularly in the case of the nitrate, when excess of the acid is added to the solution:

$$Fe(NO_3)_3 + 3H_2O \leftrightarrows Fe(OH)_3 + 3HNO_3.$$

Ferric iodide is reduced by the hydriodic acid produced by its own hydrolysis, and hence ferrous iodide does not unite with iodine to form this compound. The case is similar to that of cupric iodide (p. 788).

Ferric hydroxide $Fe(OH)_3$ appears as a brown precipitate when a base is added to a ferric salt. It does not interact with excess of the alkali. In this form the substance dries to the oxide without giving definite intermediate hydrated oxides. The hydrates, $Fe_2O_3,2Fe(OH)_3$ (brown iron ore) and $Fe_2O_3,4Fe(OH)_3$ (bog iron ore), however, are found in nature. The hydroxide passes easily into colloidal suspension in a solution of ferric chloride, and by subsequent dialysis through a piece of parchment the bulk of the salt can be separated, and an almost pure colloidal suspension of the hydroxide obtained. The hydroxide is a positive colloid and is coagulated (brown precipitate) by the addition of salts, bivalent negative ions being more effective than univalent ones (p. 642).

Ferric oxide, Fe_2O_3, is sold as "rouge" and "Venetian red." It is made from the ferrous sulphate obtained in cleaning iron ware which is to be tinned or galvanized (see p. 746). The salt is allowed to oxidize, and the ferric hydroxide, thrown down by the addition of lime, is calcined. The product varies in tint from a bright yellowish-red to a dark violet-brown according to the fineness of the powder. The best rouge is obtained by calcining ferrous oxalate FeC_2O_4. This oxide is not distinctly acidic, but by fusion with more basic oxides, compounds like franklinite $Zn(FeO_2)_2$ may be formed. It is reduced by hydrogen, at about 300° to ferrous oxide, and at 700–800° to metallic iron.

Magnetic oxide of iron Fe_3O_4 or lodestone is found in nature, and is formed by the action of air (hammer-scale), steam, or carbon dioxide on iron. It forms octahedral crystals like the spinelles, (p. 772), and is a ferrous-ferric oxide FeO,Fe_2O_3 or $Fe(FeO_2)_2$, related to franklinite.

Ferric sulphide Fe_2S_3 may be made by fusing together the free elements, and is obtained also as a precipitate by the addition of ammonium sulphide to ferric chloride solution. With hydrogen sulphide, only sulphur is thrown down (compare p. 904).

Ferric sulphate $Fe_2(SO_4)_3$ is formed by oxidation of ferrous sulphate, and is obtained as a white mass by evaporation. It gives alums (p. 774), such as ferric-ammonium alum $(NH_4)_2SO_4,Fe_2(SO_4)_3,24H_2O$, which are almost colorless when pure, but usually have a pale reddish-violet tinge.

Pyrite. — The mineral pyrite FeS_2 (Fools' gold) is the sulphide of iron which is most stable in the air. It is not attacked by dilute acids, but concentrated hydrochloric acid slowly converts it into ferrous chloride and sulphur. It is reduced by hydrogen to ferrous sulphide.

Cyanides. — When potassium cyanide is added to solutions of ferrous or ferric salts, yellowish precipitates are produced, but the simple cyanides cannot be obtained in pure form. These precipitates interact with excess of the cyanide giving soluble complex cyanides. These are called ferro- and ferricyanide of potassium, respectively.

Ferrocyanide of potassium $K_4Fe(CN)_6,3H_2O$, "yellow prussiate of potash," is made by heating nitrogenous animal refuse, such as blood, with iron filings and potassium carbonate. The resulting mass contains potassium cyanide and ferrous sulphide, and when it is treated with warm water these interact and produce the ferrocyanide:

$$2KCN + FeS \rightarrow Fe(CN)_2 + K_2S,$$
$$4KCN + Fe(CN)_2 \rightarrow K_4.Fe(CN)_6.$$

The trihydrate forms large, yellow, monosymmetric tables. Its aqueous solution contains almost exclusively the ions K^+ and $Fe(CN)_6^{====}$, and gives none of the reactions of the ferrous ion Fe^{++}. One of the double decompositions of this salt — namely, that with ferric salts — is important because it gives a gelatinous precipitate of **Prussian blue** (ferric ferrocyanide):

$$4FeCl_3 + 3K_4Fe(CN)_6 \rightarrow Fe_4^{III}(Fe(CN)_6)_3^{IV} \downarrow + 12KCl.$$

Prussian blue is employed in making paints, and is the usual pigment in **laundry blueing.** Although insoluble, it is such a fine powder that it appears to dissolve in the water. It is used in the laundry to correct the yellowish tint derived from the ferrous bicarbonate in the water (p. 732). If the goods are not freed by rinsing from soap and soda, however, the alkali liberated by hydrolysis of the latter enters into double decomposition with the Prussian blue and produces more rust:

$$Fe_4(Fe(CN)_6)_3 + 12NaOH \rightarrow 4Fe(OH)_3 \downarrow + 3Na_4Fe(CN)_6.$$

Potassium Ferricyanide $K_3^I[Fe(CN)_6]^{III}$. — The difference between this and the preceding salt can be seen by writing the formulæ thus: $4KCN,Fe(CN)_2$ and $3KCN,Fe(CN)_3$. In the ferri-

cyanide the iron is trivalent and the negative ion $Fe(CN)_6^{\equiv}$ is also trivalent as a whole. It is a soluble salt, of red color, made by oxidizing the ferrocyanide with chlorine or electrolytically (compare p. 890). With ferric salts it gives only a brown solution, but with ferrous salts it gives a deep blue precipitate of ferrous ferricyanide — **Turnbull's blue:**

$$3FeCl_2 + 2K_3Fe(CN)_6 \rightarrow Fe_3(Fe(CN)_6)_2 \downarrow + 6KCl.$$

We can *distinguish ferrous-ion* Fe^{++} from *ferric-ion* Fe^{+++} by this reaction. An equally sharp distinction is obtained by adding potassium thiocyanate, for, although the **ferrous** and **ferric thiocyanates** are both soluble, the latter is *blood red in color* (see p. 270).

It has recently been shown that the red color observed in the thiocyanate test for ferric ion is actually due to the complex ion $Fe(CNS)_6^{\equiv}$, and that ether extracts the compound $Fe[Fe(CNS)_6]$ from an aqueous solution of "ferric thiocyanate." The diminution of color produced by the addition of ammonium chloride (p. 271) is ascribed to the formation of a hexachloroferric ion:

$$Fe(CNS)_6^{\equiv} + 6Cl^- \rightarrow FeCl_6^{\equiv} + 6CNS^-.$$

Blue-Prints. — Some ferric salts are reduced to ferrous salts when exposed to light. Thus ferric oxalate $Fe_2(C_2O_4)_3$ will keep in the dark, but in light gives ferrous oxalate FeC_2O_4:

$$Fe_2(C_2O_4)_3 \rightarrow 2FeC_2O_4 + 2CO_2 \uparrow.$$

When paper is dipped in ferric oxalate solution and dried, and a fern (or ink drawing on transparent paper) is placed over the prepared sheet, sunlight will reduce the iron to the ferrous condition excepting where the fern or ink lines protect it from the light. When the sheet is now dipped in potassium ferricyanide solution (developer), the ferric oxalate gives only a brown substance which can be washed out. But the parts exposed to the light turn deep blue from the precipitation of ferrous ferricyanide in the paper. The pattern is white on a blue ground. In regular blue-print paper ammonium-ferric citrate takes the place of the oxalate, and the ferricyanide has already been applied to the paper, so that only exposure and washing remain to be done.

The student may make blue-prints for his own use as follows. Dissolve 10 g. of potassium ferricyanide in 100 c.c. of water, and 13 g. of ammonium-ferric citrate in a second 100 c.c. Mix equal volumes of the two solutions and

filter if there is any precipitate. Paint evenly over the paper with a clean camel's-hair brush, dry, and keep in a dark place until required.

Ink. — Writing ink is commonly made by adding ferrous sulphate to an extract of nut-galls. The active component of this extract is tannic acid, useful also in dyeing (p. 648) and in tanning leather (p. 878). Tannic acid is not, strictly speaking, a single substance, but a mixture of complex phenolic acids (see p. 587). Ferrous tannate is soluble and almost colorless, but is slowly oxidized, when exposed to air, to the insoluble, black ferric tannate. To make the writing visible from the first, a blue or black dye is added to the ink.

Stains of fresh writing ink, being soluble, can usually be washed out with water, if the latter is used at once. After the oxidation has occurred, the ferric tannate must be reduced again, by soaking the part for 12 hours or longer in ammonium oxalate solution, and the ink can then be washed out. Rust stains are often rendered soluble by ammonium oxalate also.

Iron Carbonyls. — When carbon monoxide is led over finely divided iron at 40–80°, or under eight atmospheres pressure at the ordinary temperature, volatile compounds of the composition $Fe(CO)_4$, **iron tetracarbonyl,** and $Fe(CO)_5$, the **pentacarbonyl,** are formed. When the gaseous mixture is heated more strongly, the compounds decompose again, and iron is deposited. Illuminating-gas burners frequently receive a deposit of iron from this cause.

Ferrates. — A red solution of potassium ferrate K_2FeO_4 is obtained by passing chlorine through caustic potash in which ferric hydroxide is suspended, or by heating pulverized iron with dry sodium nitrate. The salt crystallizes in red, rhombic prisms, isomorphous with the sulphate and chromate of potassium. It alters quickly in solution, in consequence of hydrolysis and subsequent decomposition of the ferric acid, depositing ferric hydroxide and giving off oxygen. Barium, strontium, and calcium salts are formed as red precipitates by double decomposition.

Analytical Reactions of Compounds of Iron. — There are two ionic forms of iron, ferrous-ion Fe^{++}, which is very pale-green, and ferric-ion Fe^{+++}, which is almost colorless. The yellow color of ferric salts is due to hydrolysis. Ammonium sulphide gives with the former black ferrous sulphide, which is soluble in dilute acids. The hydroxides are white and brown, respectively. With ferrocya-

nide of potassium, ferrous salts give a white, and ferric salts a blue precipitate. With ferricyanide of potassium the former gives a deep-blue precipitate, and the latter a brown solution. Ferric thiocyanate $Fe(CNS)_3$ is deep-red (p. 270). With borax, iron compounds give a bead which is green (ferrous borate) in the reducing flame, and colorless or, with much iron, yellow (ferric borate) or even brown when oxidized.

Cobalt Co and Nickel Ni

In olden times ores containing cobalt and nickel were frequently mistaken for iron and copper ores, and were treated accordingly. Failure to isolate the expected metals was regarded as due to supernatural influences, hence the word *cobalt* is derived from the German *Kobold,* an evil spirit (akin to the English "goblin"), while the connection between *nickel* and the chief of evil spirits is obvious. Cobalt continued to justify its name until very recently; only within the last few years have any applications of the metal been discovered. Nickel, on the other hand, has long ago found many uses.

The Chemical Relations of Cobalt. — Cobalt forms cobaltous and cobaltic oxides and hydroxides CoO and $Co(OH)_2$, Co_2O_3 and $Co(OH)_3$ respectively, which are all basic, the former more so than the latter. Cobalt dioxide CoO_2, however, is acidic, forming cobaltites. The cobaltous salts are little hydrolyzed, but the cobaltic salts are largely decomposed by water. The latter also liberate readily one-third of the negative radical, after the manner of manganic salts, becoming cobaltous. Complex cations and anions containing cobalt are very numerous and very stable.

Occurrence and Properties. — Cobalt is found along with nickel in **smaltite** $CoAs_2$, and **cobaltite** $CoAsS$. The pure metal may be made by Goldschmidt's process, or by reducing an oxide with hydrogen. The metal is silver-white, with a faint suggestion of pink. It displaces hydrogen slowly from dilute acids, but interacts readily with nitric acid.

An alloy of cobalt, chromium and tungsten (**stellite**) is used for high-speed tools. When heated, it keeps its temper even better than the special steel alloys (p. 902).

Cobaltous Compounds. — The chloride $CoCl_2,6H_2O$ may be made by treating the oxide with hydrochloric acid. It forms red prisms, and when partially or completely dehydrated becomes deep-blue. Writing made with a diluted solution upon paper is almost invisible, but becomes blue when warmed and afterwards takes up moisture from the breath, and is once more invisible (**sympathetic ink**). Most cobaltous compounds are red when hydrated or in solution (CO^{++}), and blue when dehydrated. By addition of sodium hydroxide to a cobaltous salt, a blue basic salt is precipitated. When the mixture is boiled, the pink **cobaltous hydroxide** $Co(OH)_2$ is formed. This becomes brown through oxidation by the air. It interacts with ammonium hydroxide, giving a soluble ammonio-cobaltous hydroxide, which is quickly oxidized by the air to an ammonio-cobaltic compound (see p. 912). It dissolves also in salts of ammonium as does magnesium hydroxide (p. 743). When dehydrated it leaves the black **cobaltous oxide** CoO. The black **cobaltous sulphide** CoS is precipitated by ammonium sulphide from solutions of all salts, and even by hydrogen sulphide from the acetate. A sort of **cobalt glass,** made by fusing sand, cobalt oxide, and potassium nitrate, forms, when powdered, a blue pigment, **smalt,** used in china-painting and by artists.

Cobaltic Compounds. — By addition of a hypochlorite to a solution of cobaltous salt, **cobaltic hydroxide** $Co(OH)_3$, a black powder, is precipitated. Cautious ignition of the nitrate gives **cobaltic oxide** Co_2O_3. Stronger ignition gives the commercial oxide, which is a **cobalto-cobaltic oxide** Co_3O_4. Cobaltic oxide dissolves in cold hydrochloric acid, but the solution gives off chlorine when warmed.

Complex Compounds. — Potassium cyanide precipitates from cobaltous salts a brownish-white cyanide. This interacts with excess of the reagent, giving a solution of **potassium cobaltocyanide** $K_4.Co(CN)_6$ (compare p. 907). This compound is easily oxidized by chlorine, or even when the solution is boiled in the air, and the colorless **potassium cobalticyanide** is formed:

$$4K_4Co(CN)_6 + 2H_2O + O_2 \rightarrow 4K_3.Co(CN)_6 + 4KOH.$$

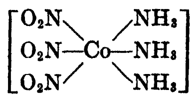
The solution gives none of the reactions of Co^{+++}, and with acids the very stable cobalticyanic acid, $H_3Co(CN)_6$, is liberated.

When acetic acid and potassium nitrite are added to a cobaltous salt, the latter is oxidized by the nitrous acid (liberated by the

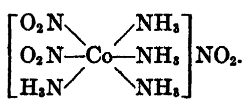
acetic acid) and a yellow complex salt $K_3.Co(NO_2)_6$, **potassium cobaltinitrite,** is thrown down.

Cobaltic salts give with ammonia complex compounds which are many and various. The cations often contain negative groups and are such as $Co(NH_3)_6{}^{+++}$, $Co(NH_3)_5Cl^{++}$ and $Co(NH_2)_5NO_2{}^{++}$. Usually the solutions give none of the reactions of cobaltic ions, and often fail likewise to give those of the anion of the original salt.

Cobaltic nitrite $Co(NO_2)_3$ combines with three molecules of ammonia to form the molecular compound $Co(NO_2)_3,3NH_3$. The co-ordination number of cobalt being six on the Werner theory, we assign to this compound the formula:



and we perceive that there are *no outside atoms or radicals* available for ionization. The compound is, indeed, practically a non-electrolyte in aqueous solution. However, the compound readily combines with another molecule of ammonia, and in so doing expels one of its nitrite radicals from the nucleus. This group is now reactive, and can be set free as nitrous acid on addition of dilute acids. The new compound also shows a conductivity in dilute aqueous solution corresponding to that of a uni-univalent salt of the type NaCl. Its formula is consequently written:



The same process can be repeated, and the absorption of another molecule of ammonia gives a compound, the formula of which may be written $[Co(NO_2)\text{-}NH_3)_5](NO_2)_2$, in accordance with the fact that its conductivity in dilute aqueous solution corresponds to that of a bi-univalent salt of the type $CaCl_2$. And finally, the addition of still another molecule of ammonia expels the last nitrite radical from the nucleus, giving the compound $[Co(NH_3)_6](NO_2)_3$, the conductivity of which in dilute aqueous solution corresponds to that of a tri-univalent salt of the type $FeCl_3$.

The Chemical Relations of Nickel. — Nickel forms nickelous oxide and hydroxide NiO and $Ni(OH)_2$, nickelic oxide Ni_2O_3 and nickel dioxide NiO_2. Only the former are basic, the nickelous salts resembling the cobaltous and ferrous salts, but not being oxidizable into corresponding nickelic compounds. Since there are no nickelic salts, there are here no analogues of the cobalticyanides or the cobaltinitrites. The complex nickelous salts, like the complex cobaltous salts, and unlike the complex cobaltic salts, are unstable,

and so give some of the reactions of Ni^{++}. Nickel dioxide is slightly acidic, and a few nickelites have been prepared.

Occurrence and Properties. — Nickel occurs free in meteorites. It is now manufactured chiefly from **pentlandite** [Ni,Cu,Fe]S, found at Sudbury (Ontario), and from **garnierite,** a silicate of nickel and magnesium, found in New Caledonia. In the former case, the ore is roasted, smelted, and finally bessemerized. The resulting alloy of copper and nickel is much used for sheet-metal work (**Monel metal,** approx. 1 : 1). Pure nickel is separated from the copper by an electrolytic process (p. 794), or by the Mond process (see p. 914).

The metal is white, with a faint tinge of yellow, is very hard, and takes a high polish (m.-p. 1452°). It is extensively used in making steel and other alloys, such as German silver (copper, zinc, nickel, 2 : 1 : 1) and the "nickel" used in coinage (copper, nickel, 3 : 1). Nickel plating on iron is accomplished exactly like silver plating (p. 809). The bath contains an ammoniacal solution of ammonium-nickel sulphate $(NH_4)_2SO_4,NiSO_4,6H_2O$, and a plate of nickel forms the anode.

The metal rusts very slowly in moist air. It displaces hydrogen with difficulty from dilute acids, but interacts with nitric acid.

Compounds of Nickel. —The **chloride** $NiCl_2,6H_2O$ is made by treating any of the oxides with hydrochloric acid, and is green in color (when anhydrous, brown). The **sulphate** $NiSO_4,6H_2O$ is the most familiar salt. **Nickelous hydroxide** $Ni(OH)_2$ is formed as an apple-green precipitate, and when heated leaves the green **nickelous oxide** NiO. It dissolves in ammonium hydroxide, giving a complex nickel-ammonia cation. It is soluble also in salts of ammonium (compare p. 911). By cautious ignition of the nitrate, **nickelic oxide** Ni_2O_3 is formed as a black powder. The oxides and salts, when heated strongly in oxygen, give the oxide Ni_3O_4. The last two oxides liberate chlorine when treated with hydrochloric acid, and give nickelous chloride. **Nickelic hydroxide** $Ni(OH_3$ is a black precipitate formed when a hypochlorite is added to any salt of nickel. **Nickelous sulphide** is thrown down by ammonium sulphide, and behaves like cobaltous sulphide (p. 911).

Addition of **dimethylglyoxime** to an ammoniacal solution of a salt of nickel gives a brilliant scarlet precipitate of **an acid salt:**

$$Ni(OH)_2 + 2(HON)_2C_2(CH_3)_2 \rightarrow 2H_2O + NiH_2[C_2N_2O_2(CH_3)_2]_2.$$

No precipitate with this organic reagent is given by salts of cobalt.

With potassium cyanide and a salt of nickel the greenish **nickelous cyanide,** $Ni(CN)_2$, is first precipitated. This dissolves in excess of the reagent, and a complex salt $K_2Ni(CN)_4,H_2O$ may be obtained from the solution. This salt is of different composition from the corresponding compounds of cobalt and of iron, and is less stable. Thus, with bleaching powder, it gives $Ni(OH)_3$ as a black precipitate. When the solution is boiled in the air no oxidation to a complex nickelicyanide occurs, and indeed no such salts are known. This fact enables the chemist to separate cobalt and nickel, for when the mixed cyanides are boiled and then treated with bleaching powder, the cobalticyanide is unaffected. With potassium nitrite and acetic acid no insoluble compound corresponding to that given by cobalt salts is formed by salts of nickel. This action also is used for the purpose of separation.

When finely divided nickel, made by reducing the oxide or oxalate with hydrogen at a moderate temperature, is exposed to a stream of cold carbon monoxide, **nickel carbonyl** $Ni(CO)_4$ is formed. This is a vapor and is condensable to a colorless liquid (b.-p. 43° and m.-p. —25°). The vapor is poisonous. When heated to 150–180° it is dissociated and nickel is deposited. Cobalt forms no corresponding compound. Commercially, pure nickel is separated from copper (and cobalt) in the **Mond process** by passing carbon monoxide over the pulverized alloy, and subsequently heating the gas.

Analytical Reactions of Compounds of Cobalt and Nickel. — The cobalt ion Co^{++} is pink, and the nickelous ion Ni^{++} green. The reactions used in analysis have been described in the preceding paragraphs. With borax, cobalt compounds give a blue bead (cobaltous borate), and nickel compounds a bead which is brown in the oxidizing flame and cloudy, from the presence of gray, metallic nickel, when reduced.

Exercises. — 1. What would be the interactions of calcium carbonate when fused with sand and with clay, respectively?

2. Make equations representing, (*a*) the oxidation of ferrous chloride by air, (*b*) the hydrolysis of ferrous carbonate and the oxidation of ferrous hydroxide, (*c*) the oxidation of ferrous sulphate in the presence of sulphuric acid by hypochlorous acid, (*d*) the reduction of ferric chloride by iron and by hydrogen sulphide, respectively, (*e*) the formation of ferric ferrocyanide and of ferrous ferricyanide.

3. Explain the solubility of cobaltous and nickelous hydroxide in salts of ammonium.

4. Construct equations to show the formation, (*a*) of the insoluble potassium cobaltinitrite (nitric oxide is given off), (*b*) of nickelic hydroxide from nickelous chloride and sodium hypochlorite. Remembering that the hypochlorite is somewhat hydrolyzed, explain why the precipitation in (*b*) is complete.

5. Tabulate in detail the chemical relations of the elements cobalt and nickel, with especial reference to showing the resemblances and differences.

6. How could you demonstrate that ferric hydroxide is in colloidal suspension in water, and not dissolved?

7. Construct the equilibrium curve for the reaction: $Fe_3O_4 + CO \rightleftarrows 3FeO + CO_2$ from the following data. Plot temperature vertically and percentage composition of furnace gases horizontally.

Temperature (°C.)	350	400	450	500	550	600	700	900
% CO_2 by volume	69	59	54	53	56	60	67	76

8. Which is the stable oxide under each of the following conditions: (*a*) 500° and 60 per cent CO_2; (*b*) 500° and 50 per cent CO_2; (*c*) 700° and 60 per cent CO_2? What will happen to FeO at 600° and 70 per cent CO_2?

9. Construct the equilibrium curve for the reaction: $FeO + CO \rightleftarrows Fe + CO_2$ from the following data. Plot as in Exercise 7.

Temperature (°C).	500	550	600	650	700	750	850	950
% CO_2 by volume	32	37	40	42	42	40	33	24

10. What will occur to FeO at 650° when the furnace gases contain (*a*) 35 per cent CO_2; (*b*) 50 per cent CO_2; (*c*) 70 per cent CO_2?

11. Construct the equilibrium curve for the reaction: $C + CO_2 \rightleftarrows 2CO$ at 1 atm. pressure from the following data. Plot as in Exercise 7.

Temperature (°C.)	450	550	600	650	700	750	800	900
% CO_2 by volume	98	90	77	61	42	25	7	3

12. Is carbon monoxide stable or unstable under the following conditions: (*a*) 600° and 50 per cent CO_2; (*b*) 750° and 50 per cent CO_2? Will carbon react with carbon dioxide at (*a*) 800° and 10 per cent CO_2, (*b*) 450° and 90 per cent CO_2?

13. Why does the percentage of CO_2 in the equilibrium mixture fall off as the temperature rises (p. 366)? What effect would increase of pressure have upon the point of equilibrium at any given temperature (p. 285)? Would increase of pressure affect the curves in Exercises 7 and 9 significantly? If not, why not?

14. Plot the curves for the three reactions discussed above all on one diagram. Under what conditions (temperature and percentage of CO_2 in furnace gases) would reduction of Fe_3O_4 to FeO occur in the blast furnace, if equilibrium was maintained in reactions 1 and 3? Under what conditions would reduction of FeO to Fe occur, if equilibrium was maintained in reactions 2 and 3?

15. If the furnace gases issue from the blast furnace at a temperature of 500°, what percentage of carbon monoxide should they contain? Would a gas with this composition be combustible? How then do you explain the fact that the issuing gases are used industrially for heating purposes?

16. What volume of hydrogen at 15° and 750 mm. will be obtained by the action of excess sulphuric acid on 100 g. of manganese steel, analyzing 90% Fe, 9% Mn and 1% C?

17. What volume of chlorine at 15° and 750 mm. will be required to oxidize 1 liter of a normal solution of ferrous chloride to ferric chloride?

18. Balance the following equations by the ion and electron method:

$$(a)\ FeSO_4 + O_2 + H_2O \rightarrow Fe(OH)SO_4$$
$$(b)\ FeCl_3 + SnCl_2 \rightarrow FeCl_2 + SnCl_4.$$

19. What are the percentage compositions of $Fe_4(Fe(CN)_6)_3$ and $Fe_3(Fe(CN)_6)_2$ respectively? Name each substance and justify its nomenclature.

20. Write in detail the equations for all the reactions involved in the making of blue-prints (p. 908).

21. Balance the following equations by the ion and electron method:

$$(a)\ Co_2O_3 + HCl \rightarrow CoCl_2 + H_2O + Cl_2$$
$$(b)\ K_4Co(CN)_6 + H_2O + O_2 \rightarrow K_3Co(CN)_6 + KOH.$$

22. How would you prove that the complex ion $Ni(CN)_4^=$ is much less stable than the complex ion $Co(CN)_6^=$?

23. How would you separate a mixture of finely-powdered nickel, cobalt and copper into its components?

24. Re-explain the color changes induced in a mixture of dilute ferric chloride and ammonium thiocyanate solutions by addition of various salts (p. 270) in the light of the new evidence brought forward on p. 908.

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CHAPTER LIII

PRACTICAL REVIEW OF THE METALLIC ELEMENTS

As in Chapter XL, so here, we assume that the specimen to be identified contains a single substance. We consider first the metallic elements, and limit ourselves to the more common of those that have been described in the context. Our review will cover, mainly, the properties of each simple metallic positive radical.

Although arsenic is predominantly a non-metallic element, and antimony is partially non-metallic, it is more convenient in the problem of recognition to classify them with the metallic elements.

External Examination. — The **color** is often significant. Most of the common compounds of iron, nickel, cobalt, copper, gold, manganese and chromium are colored (see text). A **metallic luster** (scrape off the tarnish) usually, though not always, indicates a free metal or an alloy. The **crystalline form** should be noted. The **odor** usually gives information about non-metallic constituents (p. 673) only. As regards **state,** the vast majority of the metals and their compounds are **solids.** When a **liquid** presents itself, therefore, it is usually an aqueous solution of some compound. Obtain the solid by evaporation.

Solubility and Reaction of the Solution. — Ascertain whether the substance is **soluble** in water (table on inside front cover). Note whether the solution is **acid, alkaline,** or **neutral** in reaction (p. 408). No substance can be identified by the preceding observations alone, but the final conclusion as to the nature of the specimen must be in harmony with them.

A salt which gives an acid reaction must be an acid salt of a polybasic acid (p. 405), or a derivative of a strong acid and a weak base. Similarly a salt which reacts alkaline must be a *basic salt,* or a derivative of a weak acid and a strong base.

Recognition by Reactions in Solution. — Starting with the substance in solution, its identity can be ascertained by using reactions involving mainly precipitations and oxidations or reductions, which separate the metals into five distinct **groups.**

The following plan, taken in conjunction with the statements in the context, shows how *a single cation* may be identified. What will be said applies only to the case of a solution containing salts like the chlorides, nitrates, or sulphates of one or more cations, and leaves the oxalates, phosphates, cyanides, and some other salts out of consideration.

Before attempting to understand this plan, the student should turn to the discussion on *ionic equilibria* (Chapter XLIV) and read it carefully through. The sections on the *solubility of precipitates* (pp. 760–3) should be particularly studied, since upon the principles therein formulated the whole plan is directly based.*

Group I. — Add to the solution hydrochloric acid. A precipitate indicates that cations giving insoluble chlorides are present. Silver, mercurous and lead salts give the white AgCl, HgCl, and $PbCl_2$ respectively. The last-named salt, being appreciably soluble, will be only incompletely precipitated.

These three chlorides can be distinguished from one another very easily. When excess of ammonium hydroxide is added to the precipitate, *silver* chloride *dissolves* (p. 807). *Mercurous* chloride *turns black*, owing to the formation of a finely divided mixture of free mercury and mercuric amidochloride $Hg(NH_2)Cl$. *Lead* chloride remains apparently *unchanged.*

Group II. — If no precipitate appears on addition of hydrochloric acid, hydrogen sulphide is led into the solution. The sulphides insoluble in strong acids, namely, HgS, CuS, PbS, Bi_2S_3, CdS, As_2S_3, Sb_2S_3, SnS, are therefore thrown down. The first four are black or dark brown, the next two are yellow, and the last two are orange and brown respectively. If too much HCl is present, the precipitation of several of these sulphides will be incomplete. On the other hand, if too little HCl is used, zinc sulphide may be partially precipitated (see pp. 409, 760).

This group is readily *sub-divided.* The last three sulphides pass into solution when warmed with yellow ammonium sulphide, for they give soluble *complex sulphides.* The first five sulphides will be unaffected.

* **Many experimental details, essential for the successful performance of the tests described in this chapter, are here omitted. They will be found in the Author's *Laboratory Outline of Smith's College Chemistry.***

Group IIa. — HgS, CuS, PbS, Bi_2S_3, CdS. A *yellow* precipitate insoluble in ammonium sulphide indicates *cadmium*. To distinguish between the remaining four sulphides, boil with HNO_3; *HgS* alone does *not* go into solution. Dilute the solution, and add H_2SO_4. *Lead* gives a *white precipitate* of $PbSO_4$. If no precipitate is obtained, add NH_4OH till alkaline. *Bismuth* gives a *white precipitate of* $Bi(OH)_3$, *copper* a *blue solution.*

Group IIb. — As_2S_3, Sb_2S_3, SnS. The color distinction is not always certain. Reprecipitate the sulphides by adding HCl, and boil the precipitate with concentrated HCl. As_2S_3 does *not* dissolve. If the precipitate does dissolve, cool the solution and place in it a piece of bright tin. A *black deposit* forming on the surface (by displacement, see p. 313) indicates Sb. *No deposit* indicates Sn.

Group IIIa. — If no precipitate was obtained with H_2S, the solution is boiled, and a few drops of concentrated HNO_3 added to oxidize any *ferrous* salt to the *ferric* state. Ammonium chloride is added, and then ammonium hydroxide *in excess*. A *white, gelatinous* precipitate of $Al(OH)_3$ indicates *aluminium*, a *bluish-green* precipitate of $Cr(OH)_3$ indicates *chromium*, a *reddish-brown* precipitate of $Fe(OH)_3$ indicates *iron*. The presence of NH_4Cl is necessary to reduce the concentration of OH^- furnished by the NH_4OH below the point at which other less insoluble hydroxides (such as $Mn(OH)_2$) would be precipitated. To tell whether iron was originally present in the ferrous or the ferric condition, the *ferricyanide test* (p. 908) should be applied.

Group IIIb. — If, still, no precipitate is obtained, hydrogen sulphide is led into the *alkaline* solution. Sulphides which are insoluble in water, but soluble in strong acids (see pp. 409, 763), now appear. They are CoS and NiS (both black), MnS (flesh-colored) and ZnS (white). To distinguish between Co and Ni, add NaOH to the original solution. *Cobalt* gives a *blue* precipitate of a basic salt, changing to *pink* $Co(OH)_2$ on boiling; *nickel* gives a *light-green* precipitate of $Ni(OH)_2$.

Group IV. — If negative results are still obtained, add $(NH_4)_2CO_3$. A white precipitate is given by three of the remaining metals, whose carbonates are insoluble, *calcium, strontium* and *barium*. Distinction between these three may be made by the *flame test*. A small portion of the precipitate is taken up on a

platinum wire and held in the Bunsen flame. A *brick-red* coloration signifies Ca, a *crimson-red* Sr, a *green* Ba.

Group V. — The only other common positive radicals are Mg, NH_4, K and Na. On addition of ammonium phosphate to the solution from Group IV, *magnesium,* if present, is precipitated in the form NH_4MgPO_4 (white). An ammonium salt may be recognized by boiling some of the original solution with NaOH, when *ammonia* is evolved. *Potassium* salts confer a *violet* coloration to the Bunsen flame; *sodium* salts a *bright yellow.*

Confirmatory Tests. — From the context in earlier chapters, the student will be able to pick out for each particular metal other tests which may serve to confirm the conclusions arrived at in the course of the above analysis. Often the metallic radical can be recognized by a *displacement* reaction (compare pp. 793, 802). Often, again, *color changes* which occur during the course of the scheme of operations outlined above give indications of value. Thus a *yellow* solution changing to *green* during the passage of H_2S in Group II signifies a chromate (p. 877), a *purple* solution becoming *colorless* signifies a permanganate (p. 891). The borax and microscosmic salt bead colorations (see pp. 554, 668) also supply exceedingly valuable confirmatory evidence in many cases.

Tests for Negative Radicals. — Precipitation reactions similar in nature to those outlined above may be utilized as additional tests for the negative radical of an unknown substance (see Chapter XL). Thus a *chloride* gives with *silver nitrate* a *white* precipitate, soluble in ammonia. A *sulphate* gives a *white* precipitate with *barium chloride,* insoluble in hydrochloric acid. From the context, the student will be able to discover for himself confirmatory tests of this kind for most of the common negative radicals discussed in this book. For a complete scheme, however, a manual of qualitative analysis should be consulted.

The following simple compounds are soluble, but are so little ionized that their solutions do not show all the reactions of both of the ions: NH_4OH, H_2S, HCN, H_2CO_3, $HgCl_2$, $Hg(CN)_2$, $Fe(NCS)_3$, $Pb(C_2H_3O_2)_2$. With a number of others, for example CdI_2, the actions are incomplete for the same reason. Complex compounds, as we have seen, give complex ions, and these ions are usually so little resolved into simpler ions that the latter cannot be discovered by all the usual tests. Thus: $KAg(CN)_2$ gives K^+ and $Ag(CN)_2^-$, but very little Ag^+ and CN^- (p. 807); $Cu(NH_3)_4Cl_2$ gives much $Cu(NH_3)_4^{++}$ and Cl^-, but very little Cu^{++}. The individual cases are described in the context.

Insoluble Substances. — If the unknown substance is insoluble in water, try to bring it into solution by boiling successively with dilute HNO_3, concentrated HNO_3, and *aqua regia* (p. 533). In case it dissolves, evaporate off the excess of acid and proceed with the analysis as above. The only common substances which are still insoluble are: the sulphates of Pb, Sr, Ba; certain mineral oxides such as Al_2O_3, Cr_2O_3, Fe_2O_3, SnO_2; some silicates; CaF_2; AgCl (soluble in NH_4OH). Fuse with Na_2CO_3 in a crucible, cool, extract with water, and filter.

The *residue* contains the *positive radical* as carbonate, and may be analyzed for this after dissolving in HNO_3. The *filtrate* contains the *negative radical* as sodium salt, and may be examined as in Chapter XL.

Exercises. — 1. Name some substances that have a metallic luster, but are not metals or alloys.

2. Name the metals whose salts with active acids will give: (*a*) neutral aqueous solutions; (*b*) acid aqueous solutions. What classes of salts will give alkaline solutions?

3. Write full ionic equations for the chloride precipitations mentioned in Group I. Why is silver chloride soluble in ammonia?

4. Write full ionic equations for the sulphide precipitations mentioned in Group II. Which is the more soluble in water, mercuric sulphide or cadmium sulphide?

5. Write full ionic equations for the hydroxide precipitations mentioned in Group IIIa. Which is the more soluble in water, aluminium hydroxide or magnesium hydroxide?

6. Write full ionic equations for the sulphide precipitations mentioned in Group IIIb. Which is the more soluble in water, nickel sulphide or zinc sulphide?

7. Write full ionic equations for the carbonate precipitations mentioned in Group IV.

8. Write full ionic equations for the reactions mentioned in Group V.

9. Give a precipitation test for the negative radical in each of the following substances: sodium hydroxide, potassium carbonate, sodium sulphide, sodium phosphate. Write full ionic equations in each case.

10. Tabulate the metals which could be identified by means of borax bead tests, naming the compound formed and its color in each case.

APPENDIX

I. The Metric System

Length. 1 meter (1 m.) = 10 decimeters = 100 centimeters (100 cm.) = 1000 millimeters (1000 mm).

1 kilometer = 1000 meters (1000 m.) = 0.6214 mile.

1 decimeter = 0.1 m. = 10 centimeters = 3.937 inches.

1 meter = 1.094 yards = 3.281 ft. = 39.37 in.

Volume. 1 liter = 1000 cubic centimeters (1000 c.c.) = a cube 10 cm. × 10 cm. × 10 cm.

1 liter = 0.03532 cu. ft. = 61.03 cu. in. = 1.057 quarts (U. S.) or 0.880 quarts (Brit.) = 33.8 fl. oz. (U. S.) = 35.2 fl. oz. (Brit.).

1 fluid ounce (U. S.) = 29.57 c.c. 1 fl. oz. (Brit.) = 28.4 c.c.

1 cu. ft. = 28.32 liters.

Weight. 1 gram (1 g.) = wt. of 1 c.c. of water at 4° C.* 1 kilogram = 1000 g.

1 gram = 10 decigrams = 100 centigrams (100 cg.) = 1000 milligrams (1000 mg.).

1 kilogram = 2.205 lbs. avoird. (U. S. and Brit.).

1000 kilograms = 2205 lbs. = 1 metric ton.

1 lb. avoird. = 453.6 g.

1 oz. avoird. (U. S. and Brit.). = 28.35 g.   100 g. = 3.5 oz.

II. Scale of Hardness

Each of the following minerals will scratch the surface of a specimen of any one *preceding* it in the list.

1. Talc
2. Gypsum (or NaCl)
3. Calcite (or Cu)
4. Fluorite
5. Apatite
6. Feldspar
7. Quartz
8. Topaz
9. Corundum
10. Diamond

* More accurately, 1 g. of water at 4° C. and 760 mm. pressure occupies 1.000,027 c.c. (see Exercise 18, p. 19). This volume is known as the milliliter (ml.), and is used instead of the cubic centimeter in expressing the results of very exact measurements. For most purposes, however, the error involved in the use of cubic centimeters is negligible.

Glass is slightly scratched by 5, and easily by those following. Glass will not scratch 5 distinctly, but will scratch those preceding 5.

A good **knife** scratches 6 slightly, but not those following.

A **file** will scratch 7, but not those following.

III. Temperatures Centigrade and Fahrenheit

Upon the Centigrade scale, the freezing-point of water is 0° C. and the boiling-point 100° C. Upon the Fahrenheit scale, the same

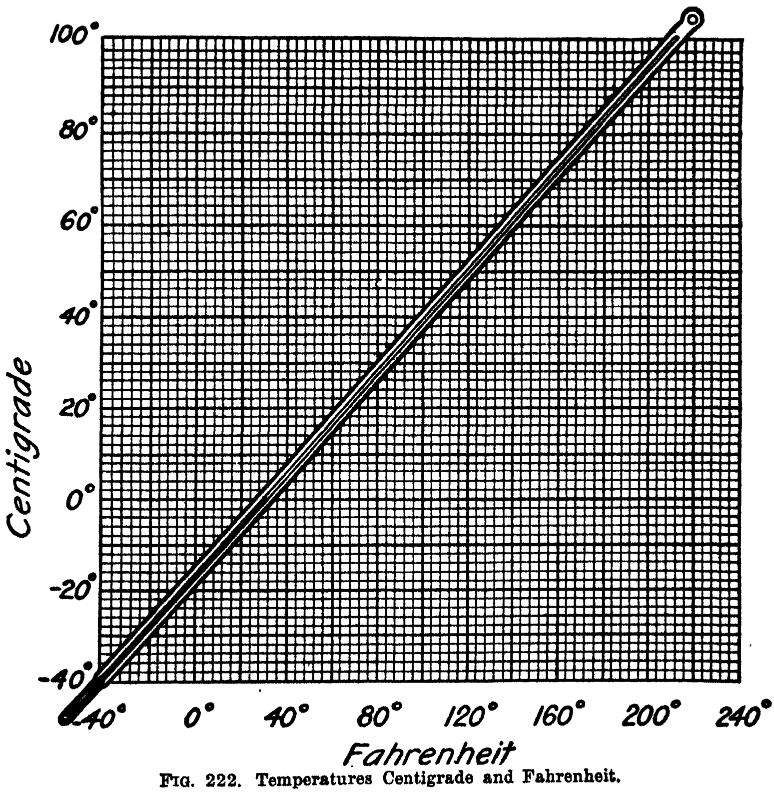


FIG. 222. Temperatures Centigrade and Fahrenheit.

points are 32° F. and 212° F., respectively. The same interval is thus 100° on the one scale and 180° on the other. The degree Fahrenheit is therefore 100/180 or 5/9 of 1° Centigrade.

The accompanying graphical representation (Fig. 222) may help to make clear the connection between the two scales.

Temperatures Fahrenheit are read horizontally and temperatures Centigrade vertically. The linear relationship exhibited in the diagram may be expressed algebraically as follows:

Let y = temperature Centigrade; x = temperature Fahrenheit.
A rise from 0° to 100° in y corresponds to a rise from 32° to 212° in x.
That is, each rise of 1 degree in y corresponds to a rise of $(212 - 32)/100 = 1.8$ degrees in x.

When $y = 0$, $x = 32$
When $y = 1$, $x = 32 + 1.8$
When $y = 2$, $x = 32 + 2(1.8)$
When $y = 100$, $x = 32 + 100(1.8)$
Or, in general, $x = 32 + 1.8\,y$.

This relationship enables us to convert temperatures Centigrade directly into temperatures Fahrenheit. To effect the reverse conversion, the expression may be transformed to:

$$1.8\,y = x - 32;\ \text{or}\ y = 5/9\,(x - 32).$$

IV. Vapor Pressures of Water

Both the Fahrenheit (F.) and the Centigrade (C.) temperatures are given.

Temperature		Pressure, mm.	Temperature		Pressure, mm.
F.	C.		F.	C.	
32°	0°	4.5	71.6°	22°	19.7
41	5	6.5	73.4	23	20.9
46.4	8	8.0	75.2	24	22.2
48.2	9	8.6	77.0	25	23.6
50.0	10	9.1	78.8	26	25.1
51.8	11	9.8	80.6	27	26.5
53.6	12	10.5	82.4	28	28.1
55.4	13	11.2	84.2	29	29.8
57.2	14	11.9	86.0	30	31.5
59.0	15	12.7	87.8	31	33.4
60.8	16	13.5	89.6	32	35.4
62.6	17	14.4	91.4	33	37.4
64.4	18	15.4	93.2	34	39.6
66.2	19	16.3	95.0	35	41.8
68.0	20	17.4	.....	...	.....
69.8	21	18.5	212.0	100	760.0

V. A List of Valences and Charges

The following table presents, for the guidance of the student, the valences of some familiar ions and the *commonest* valences of some elements. Many of these elements, however, possess other regular valences, in addition to those shown, so that the list does not pretend to be complete.

Univalent	Bivalent	Trivalent	Quadrivalent
Na^+	Ca^{++}	Al^{+++}	Sn^{++++} (stannic)
K^+	Ba^{++}	Fe^{+++} (ferric)	$(SiO_4)^{----}$
H^+	Mg^{++}	Cr^{+++}	C (CH_4, CO_2)
$(NH_4)^+$	Zn^{++}	Sb^{+++}	**Quinquivalent**
Ag^+	Pb^{++}	Bi^{+++}	N (N_2O_5)
Cl^-	Ni^{++}	$(PO_4)^{---}$	P (P_2O_5)
Br^-	Co^{++}	As (AsH_3)	As (As_2O_5)
I^-	Mn^{++}	B (B_2O_3)	**Sexivalent**
F^-	Cu^{++} (cupric)	N (NH_3, N_2O_3)	S (SO_3)
$(OH)^-$	Fe^{++} (ferrous)	P (PH_3)	
$(NO_3)^-$	Hg^{++} (mercuric)		
$(ClO_3)^-$	Sn^{++} (stannous)		
	O^{--}		
	$(SO_4)^{--}$		
	S^{--}		
	$(CO_3)^{--}$		
	O_2^{--} (peroxide)		

Where no charges are indicated, the element, by itself, does not ordinarily form an ion.

VI. Prices of Important Chemicals

The prices quoted below are current prices in the New York market for February, 1937. Quotations in other cities or at other periods may, of course, vary considerably from the figures here given, particularly under abnormal conditions such as prevailed during the depression. The student will find this table of service in considering the economic side of many industrial processes discussed in the text.

Metals	
Aluminium	23c per lb.
Antimony	12c per lb.
Arsenic	42c per lb.
Bismuth	$1 per lb.
Copper	10c per lb.
Gold	$35 per troy oz.
Lead	4.5c per lb.
Magnesium	30c per lb.
Mercury	$93 per 76 lbs.
Nickel	35c per lb.
Platinum	$53 per oz.
Silver	42c per oz.
Sodium	19c per lb.
Tin	45c per lb.
Zinc	5c per lb.

Bases	
Ammonia, anhydrous, cylinders	16c per lb.
Barium hydroxide	5c per lb.
Caustic soda, 76%	$2.60, 100 lbs.
Caustic potash	6½c per lb.
Slaked lime	85c, 100 lbs.

Oxides	
Barium peroxide	11c per lb.
Carbon dioxide, cylinders	6c per lb.
Lime (quick)	61c, 100 lbs.
Manganese dioxide	$60 per ton
Silica	$22 per ton
Sodium peroxide	20c per lb.
Sulphur dioxide, cylinders	7c per lb.
White arsenic	3½c per lb.

Miscellaneous	
Alcohol, denatured	35c per gal.
Benzene	16c per gal.
Blanc fixe	$65 per ton
Calcium carbide	5c per lb.
Carbon disulphide	5c per lb.
Carbon tetrachloride	5c per lb.
Chloroform	20c per lb.
Cream of tartar	17c per lb.
Cyanamid	$1.07 per ammonia unit
Ether	9c per lb.
Ethyl acetate	6½c per lb.
Glycerine	20c per lb.
Lithopone	4½c per lb.
Niter cake	$16 per ton
Paris green	23c per lb.

Non-Metals	
Bromine	37c per lb.
Chlorine, liquid, cylinders	5½c per lb.
Helium	3c per cu. ft.
Hydrogen	2c per cu. ft.
Iodine	$1.50 per lb.
Nitrogen	2c per cu. ft.
Oxygen	75c, 100 cu. ft.
Phosphorus (red)	40c per lb.
Sulphur, roll (mines)	$18 per ton

Acids	
Acetic acid, 56%	$4.75, 100 lbs.
Boric acid	5c per lb.
Hydrochloric, 35%	$1.35, 100 lbs.
Hydrofluoric, 30%	7c per lb.
Nitric, 56%	$5.00, 100 lbs.
Phosphoric, 50%	14c per lb.
Sulphuric, 98%	$15 per ton

Salts	
Ammonium chloride	5½c per lb.
Ammonium nitrate	4c per lb.
Ammonium sulphate	$25 per ton
Bleaching powder	$2, 100 lbs.
Borax	2c per lb.
Chrome alum	$7, 100 lbs.
Copper sulphate	4c per lb.
Epsom salts	$1.80, 100 lbs.
Ferrous sulphide	$2.50, 100 lbs.
Fluor-spar	$31 per ton
Lead acetate	11c per lb.
Potassium alum	$3.00, 100 lbs.
Potassium carbonate	7c per lb.
Potassium chlorate	9c per lb.
Potassium chloride	$22 per ton
Potassium permanganate	18c per lb.
Silver nitrate	33c per oz.
Sodium bicarbonate	$1.85, 100 lbs.
Sodium bromide	31c per lb.
Sodium carbonate	$1.20, 100 lbs.
Sodium chlorate	6c per lb.
Sodium chloride	$12 per ton
Sodium nitrate	$1.20, 100 lbs.
Sodium silicate	80c, 100 lbs.
Zinc sulphate	3c per lb.

Miscellaneous—*Continued*	
Phenol	14c per lb.
Toluene	30c per gal.
White lead	6½c per lb.

VII. Nobel Prize-winners in Chemistry

Alfred Nobel, a Swedish engineer and chemist, devoted his life to the study of explosives, especially to the manufacture and stabilization of *nitroglycerine* (pp. 652–4). Among his inventions, from which he amassed a tremendous fortune, may be mentioned dynamite, blasting gelatine, and ballistite (a precursor of cordite). Before his death, alarmed at the consequences of his discoveries, he developed into a pacifist, and planned to use his wealth to promote the advancement of civilization and the abolition of war. The bulk of his estate was accordingly bequeathed to establishing five prizes, to be awarded annually, without distinction of nationality, to such as had done mankind greatest service in each of the five fields of physics, chemistry, medicine, idealistic literature, and the promotion of peace. These prizes are now worth about $40,000 each. The awards in chemistry are tabulated below.

Year	Recipient	Chief Fields of Work
1901	J. H. Van't Hoff; Amsterdam and Berlin	Molecular structure; solutions; Stassfurt salt deposits.
1902	Emil Fischer; Berlin	Synthesis of sugars; proteins.
1903	Svante Arrhenius; Stockholm	Ionization hypothesis.
1904	Sir William Ramsay; London	Rare gases of the atmosphere.
1905	Adolph von Baeyer; Munich	Synthesis of indigo.
1906	Henri Moissan; Paris	Fluorine; electric furnace.
1907	E. Buchner; Berlin	Chemistry of fermentation.
1908	Sir Ernest Rutherford; Manchester	Radioactivity.
1909	Wilhelm Ostwald; Leipsic	Theory of solutions.
1910	O. Wallach; Göttingen	Chemistry of the terpenes.
1911	Madame Curie; Paris	Discovery of radium and polonium.
1912	V. Grignard; Nancy	Organic syntheses.
	P. Sabatier; Toulouse	Catalysis in organic chemistry.
1913	A. Werner; Zürich	Valence and chemical constitution.
1914	T. W. Richards; Harvard	Atomic weight determinations.
1915	R. Willstätter; Munich	Chlorophyll; theory of color.
1918	Fritz Haber; Berlin	Synthetic ammonia process.
1920	Walther Nernst; Berlin	Electrochemistry; thermodynamics.
1921	Frederick Soddy; Oxford	Radioactivity.
1922	F. W. Aston; Cambridge	Isotopes.
1923	F. Pregl; Graz (Austria)	Microanalysis of organic matter.
1925	R. Zsigmondy; Göttingen	Colloid chemistry.
1926	The Svedberg; Upsala	Colloid chemistry.
1927	H. Wieland; Munich	Bile acids.
1928	A. Windaus; Göttingen	Vitamins.
1929	A. Harden; London H. von Eulen-Chelpin; Stockholm	Fermentation of sugars.

1930	H. Fischer; Munich	Haemin and chlorophyll.
1931	F. Bergius; Mannheim	Hydrogenation of coal.
	K. Bosch; Oppau	Fixation of nitrogen.
1932	Irving Langmuir; Schenectady	Atomic structure, etc.
1934	H. C. Urey; New York	Discovery of deuterium.
1935	M. and Mme. Joliot-Curie; Paris	Induced radioactivity.
1936	P. Debye; Zürich	Theory of complete ionization.

VIII. Additional Reading References

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FOUR PLACE LOGARITHMS

No.	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
10	0000	0043	0086	0128	0170	0212	0253	0294	0334	0374	4	8	12	17	21	25	29	33	37
11	0414	0453	0492	0531	0569	0607	0645	0682	0719	0755	4	8	11	15	19	23	26	30	34
12	0792	0828	0864	0899	0934	0969	1004	1038	1072	1106	3	7	10	14	17	21	24	28	31
13	1139	1173	1206	1239	1271	1303	1335	1367	1399	1430	3	6	10	13	16	19	23	26	29
14	1461	1492	1523	1553	1584	1614	1644	1673	1703	1732	3	6	9	12	15	18	21	24	27
15	1761	1790	1818	1847	1875	1903	1931	1959	1987	2014	3	6	8	11	14	17	20	22	25
16	2041	2068	2095	2122	2148	2175	2201	2227	2253	2279	3	5	8	11	13	16	18	21	24
17	2304	2330	2355	2380	2405	2430	2455	2480	2504	2529	2	5	7	10	12	15	17	20	22
18	2553	2577	2601	2625	2648	2672	2695	2718	2742	2765	2	5	7	9	12	14	16	19	21
19	2788	2810	2833	2856	2878	2900	2923	2945	2967	2989	2	4	7	9	11	13	16	18	20
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	2	4	6	8	11	13	15	17	19
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	2	4	6	8	10	12	14	16	18
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	2	4	6	8	10	12	14	15	17
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	2	4	6	7	9	11	13	15	17
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	2	4	5	7	9	11	12	14	16
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2	3	5	7	9	10	12	14	15
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2	3	5	7	8	10	11	13	15
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2	3	5	6	8	9	11	13	14
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	2	3	5	6	8	9	11	12	14
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	1	3	4	6	7	9	10	12	13
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	1	3	4	6	7	9	10	11	13
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	1	3	4	6	7	8	10	11	12
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	1	3	4	5	7	8	9	11	12
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	1	3	4	5	6	8	9	10	12
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	1	3	4	5	6	8	9	10	11
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	1	2	4	5	6	7	9	10	11
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	1	2	4	5	6	7	8	10	11
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	1	2	3	5	6	7	8	9	10
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	1	2	3	5	6	7	8	9	10
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	1	2	3	4	5	7	8	9	10
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	1	2	3	4	5	6	8	9	10
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	1	2	3	4	5	6	7	8	9
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	1	2	3	4	5	6	7	8	9
43	6335	6345	6355	6365	6375	6386	6395	6405	6415	6425	1	2	3	4	5	6	7	8	9
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	1	2	3	4	5	6	7	8	9
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618	1	2	3	4	5	6	7	8	9
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	1	2	3	4	5	6	7	7	8
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	1	2	3	4	5	5	6	7	8
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	1	2	3	4	4	5	6	7	8
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	1	2	3	4	4	5	6	7	8
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	1	2	3	3	4	5	6	7	8
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	1	2	3	3	4	5	6	7	8
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1	2	2	3	4	5	6	7	7
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	1	2	2	3	4	5	6	6	7
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	1	2	2	3	4	5	6	6	7
	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9

FOUR PLACE LOGARITHMS — *Continued*

No.	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	1	2	2	3	4	5	5	6	7
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	1	2	2	3	4	5	5	6	7
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	1	2	2	3	4	5	5	6	7
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	1	1	2	3	4	4	5	6	7
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	1	1	2	3	4	4	5	6	7
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	1	1	2	3	4	4	5	6	6
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	1	1	2	3	4	4	5	6	6
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1	1	2	3	3	4	5	6	6
63	7992	8000	8007	8014	8021	8028	8035	8041	8048	8055	1	1	2	3	3	4	5	5	6
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	1	1	2	3	3	4	5	5	6
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	1	1	2	3	3	4	5	5	6
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	1	1	2	3	3	4	5	5	6
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1	1	2	3	3	4	5	5	6
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1	1	2	3	3	4	4	5	6
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1	1	2	2	3	4	4	5	6
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	1	1	2	2	3	4	4	5	6
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	1	1	2	2	3	4	4	5	5
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1	1	2	2	3	4	4	5	5
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1	1	2	2	3	4	4	5	5
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1	1	2	2	3	4	4	5	5
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1	1	2	2	3	3	4	5	5
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	1	1	2	2	3	3	4	5	5
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1	1	2	2	3	3	4	4	5
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	1	1	2	2	3	3	4	4	5
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9025	1	1	2	2	3	3	4	4	5
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	1	1	2	2	3	3	4	4	5
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1	1	2	2	3	3	4	4	5
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1	1	2	2	3	3	4	4	5
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	1	1	2	2	3	3	4	4	5
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	1	1	2	2	3	3	4	4	5
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	1	1	2	2	3	3	4	4	5
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	1	1	2	2	3	3	4	4	5
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	0	1	1	2	2	3	3	4	4
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	0	1	1	2	2	3	3	4	4
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	0	1	1	2	2	3	3	4	4
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0	1	1	2	2	3	3	4	4
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0	1	1	2	2	3	3	4	4
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0	1	1	2	2	3	3	4	4
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0	1	1	2	2	3	3	4	4
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0	1	1	2	2	3	3	4	4
95	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	0	1	1	2	2	3	3	4	4
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	0	1	1	2	2	3	3	4	4
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	0	1	1	2	2	3	3	4	4
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	0	1	1	2	2	3	3	4	4
99	9956	9961	9965	9969	9974	9978	9983	9987	9991	9996	0	1	1	2	2	3	3	3	4
	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9

INDEX

***Acids are all listed under "acid" and salts under the positive radical.